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THESIS

PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS

By

S.G.DAVIS

Edmonton, Alberta.   April,1940.

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THESIS

Phase Equilibria in Hydrocarbon Systems

Submitted in Partial Fulfilment
of the
Requirements for the degree of Master of Science

by

S.G. Davis

Under the direction of

Dr. E.H. Boomer

Time devoted to thesis work - seven months

Edmonton, Alberta April 1940

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PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS

GENERAL INTRODUCTION

The investigation of liquid-gas hydrocarbon systems has been receiving considerable and growing attention in recent years. Measurements of phase compositions and density on both simple two-component systems and the more complex systems found naturally in oil and gas wells or in the processing operations common to oil refineries have become quite extensive. Reference to the literature, as reviewed later in this thesis shows that little such work was in progress as recently as ten years ago but currently, several major investigations are under way. The information obtained is of use in correlating the behaviour of individuals in the pure state with their behaviour in complex mixtures. Formally, the information gives values for the differential coefficients in the thermodynamic equations of state and it is hoped, rules leading to the prediction of the magnitude of the coefficients. In industry, the data is of value in serving as a guide to the proper conditions for satisfactory operation of oil fields and processes concerned with mixtures of hydrocarbons.

These investigations may be divided roughly into two types, namely, those concerned with the pressure-volume-temperature behaviour of single phases of fixed composition, and those concerned with the properties and composition of two or more phases in equilibrium as a function of temperature and pressure. The present work is of the latter type.

The investigations reported in this thesis are of two kinds. There is first a study of the effects of dissolved natural gas over a range of pressures and temperatures on the behaviour of an initial single liquid phase of petroleum. Given sufficient gas in solution, the environment within the liquid phase may change to such an extent that a second liquid phase appears containing those compounds farthest removed in chemical and physical properties from the natural gas employed. The second part of this report is concerned with the equilibrium between two phases produced by contacting a light petroleum and natural gas over a range of pressures. The properties of the gas phase and the liquid phase in equilibrium and their relation to the properties of the original materials are determined and discussed.

This work is an extension of other related work being carried forward in this laboratory under the general title as used for this thesis "Phase Equilibria in Hydrocarbon Systems". Previous work has been concerned with relatively simple two-component systems and polycomponent systems of low critical pressures and temperatures. The investigations reported here represent a prelimenary examination of the highly complex systems of relatively high critical pressures and temperatures comparable to petroleum-natural gas systems found in nature.

This thesis will be presented in two sections,

Part 1

The precipitation of fractions from crude oil by the modification of a light solvent with dissolved natural gas.

Part 11

The equilibrium phase composition in systems of a composite Turner Valley crude oil and natural gas.

Part I

The precipitation of fractions from crude oil by the modification of a light solvent with dissolved natural gas.

INTRODUCTION

In general, current practice in the analysis or separation of petroleum into its components in the laboratory or plant consists essentially of a careful fractional distillation at atmospheric and reduced pressures. In addition the use of selective solvents for the separation of particular fractions is practiced, particularily with regard to the preparation of lubricating oils. Frequently, as a further aid to analysis, reactions such as nitration of aromatic compounds are taken advantage of to remove particular classes of compounds.

Excepting only in the case of the solvent method of obtaining fractions of petroleum, the methods of separation involve some chemical alteration in the materials treated. There are compounds in petroleum whose thermal behavior is such that decomposition and other reactions

occur in the most careful process of fractionation. This is especially apparent in carrying out separation of the less volatile components as occur in the lubricating oil and asphaltic portions of petroleum. Further, it is not generally possible to use a chemical reaction to remove completely a class of components without at the same time effecting reaction to some extent with other components. In contrast to these processes, selective extraction of petroleum by suitable solvents offers a method of fractionation free from any chemical reactions.

The commercial application of solvent refining processes in the recovery of lubricating oil fractions is of recent origin and phenomenal growth. A variety of solvents, sulphur dioxide, furfuraldehyde, phenol, nitrobenzene, chlorinated hydrocarbons, glacial acetic acid and propane (5, 10, 11, 14, 16, 27) have been used. They may act to extract preferentially the desired paraffinic hydrocarbons or conversely the undesired naphthenes, resins and asphalts. In either event the desired product is obtained in a quality superior to that obtained from distillation processes.

These processes are not without some disadvantages. Excepting propane, the solvents are not products of petroleum itself, or even closely related to petroleum. Some are toxic and require care in use, others, e.g. sulphur dioxide are corrosive in the presence of water and some are unstable and are subject to oxidation. The separation and recovery of the solvents is not always simple and excepting low boiling materials like propane, elevated temperatures and fractional distillation may be necessary. Finally while the extent of removal of a fraction by the solvent is controllable through the extent of extraction, most solvents are highly specific and remove only one class of components. For example a chlorinated hydrocarbon could be used for the removal of paraffin waxes from petroleums. Succeeding treatment by nitrobenzene would be required to remove asphalt and related compounds.

This investigation has as its primary objective the precipitation of successive fractions of petroleum by dissolving under successively greater and greater pressures, natural gas in petroleum. The investigation includes the use of light petroleum

fractions as solvents to increase the solubility of the gas used and permit a wider range of solvent properties. Such a process offers possibilities as an analytical tool and may have commercial applications. Extensive control of the solvent properties is afforded by control of the amount of dissolved gas. The separation of solvent and products is readily achieved under mild conditions of temperature in simple apparatus. The process can be entirely physical and the solvents are readily available. Special equipment for producing and withstanding the gas pressures required is an obvious disadvantage to commercial application but is not insup erable.

LITERATURE REVIEW

The literature offers very little information on this subject for it is a relatively new field but one which will very likely be more closely investigated in the next few years.

The use of preferential solvents in the separation of heavy oils and tars into fractions as already stated has been an established refining process in the manufacture of lubricants for some time. The possibility exists that the next step will be in the direction of controlling the action of these solvents by using varying pressures of a gas and of even using natural gas itself as a solvent.

S. Von Pilat and M. Goldewicz (18, 19, 36, 37, 38) appear to be the initial workers in this field. They used a crude oil from Polish fields for their investigation.

The first work was with petroleum residues. These were dissolved in propane and then the solvent action of the propane modified by adding natural gas (methane) under pressure. In some cases ethane was

used as the initial solvent. The heaviest components were precipitated first as a liquid phase. By progressive increase of the pressure and consequently of the quantity of the dissolved gas, fractions successively lighter and more soluble were precipitated. At a pressure of one hundred and thirty atmospheres only a small percentage of light oils remained in the propane-methane solution. Since all the fractions were liquid, very little difficulty was encountered in the separation of the phases.

Further investigation was then conducted using propane solutions of the original crude. It was also extended to solutions of crude oil and methane under high pressures.

S.V. Pilat in a further paper (39) suggests a method for the use of this process of fractional precipitation on an industrial scale. He gives the arrangement of the saturation vessels, pumps, and expansion chambers. This paper does not give any data nor does it give any probable operating conditions.

The solvent fractionation of Alberta bitumen under high pressure was investigated by M.R. Taylor(45)

In this work the bitumen was dissolved in either kerosene or gasoline before subjecting it to the pressures of methane. With solutions of sixty per cent gasoline a separation was obtained. The precipitated fractions were not analysed.

E.S. Hillman and B. Barnett have published very meager information on a method of analysis of heavy residual oils involving fractional precipitation by gaseous solution (22, 23). The oil is first treated with isopentane and the isopentane soluble portion is then dissolved in propane. With the addition of successive increments of methane to the propane solution, successive fractions of oil were precipitated from the solution. The internal pressure of the solvent varies with the methane content, decreasing with increase of pressure of methane, and this was used as a measure of solvent power. They have confined their work to the analysis of asphalts and petroleum residues and as yet have not extended it to crude stocks. The technique of fractional precipitation has not been described by these authors, only the results of its application have been published.

THEORY

The work is not new so far as the fundamental conceptions are concerned but only in its application. It is based upon the developments in solvent extraction by propane in particular, and the pioneering work of Pilat and Goldewicz (18, 19, 36, 37, 38, 39) on the modification of solvent properties by dissolved natural gas.

The broad principle "like dissolves like" of the alchemists is at the background of all extraction processes and while the theory of solutions has progressed greatly since the alchemists, the principle is still a reliable qualitative guide. Thus, an ideal solution is one that obeys Raoult's law, is an arbitrary and useful definition based on experiment. Upon examination of such solutions it is found that in general, the molecular species are very much alike. On the other hand, solutions that do not obey Raoult's law may show incomplete miscibility or at least, a maximum or minimum in the boiling point diagram. The components show marked differences in properties and molecular design.

The theory of solutions due to Hildebrand (20) based upon the concept of internal pressures serves as a useful guide of some quantitative value. The resultant of Van der Waal's forces, repulsive forces and thermal pressure gives the internal pressure. This pressure in liquids is very large and parallels directly the degree of development of dipoles in the molecules of the liquid. Given two liquids of similar internal pressure, miscibility results; if of widely different internal pressures, only partial miscibility is possible. This is the same as saying that liquids made of molecules having similar electrical structure i.e. Van der Waals forces or dipole moments are miscible, while those that are not similar will show a greater or less degree of immiscibility. Similar internal pressures may be expected from similar molecular structures. One would predict complete miscibility and obedience to Raoult's law by solutions of pentane and hexane. This pair have similar structures and low internal pressures (2020 atmospheres for n - pentane and 2140 atmospheres for n - hexane (20)) which differ relatively little. So also, benzene and toluene form

nearly perfect solutions. They have high internal pressures which are not too different, (3600 atmospheres for benzene and 2860 atmospheres for toluene (20)). The same behavior would not be expected for a pair like propane and a constituent of paraffin wax which differs greatly in molecular size and internal pressure, that for propane being very low, around one thousand atmospheres and for a paraffin wax being high, over three thousand atmospheres. Similarly, while pentane and benzene are miscible in all proportions under ordinary conditions, the solutions do not obey Raoult's law. When a sufficiently complex aromatic liquid is chosen of much higher internal pressure than benzene, the deviation from Raoult's law becomes partial miscibility. If pentane and a very different and active substance, such as asphalts, which is probably not a hydrocarbon, are brought together only slight miscibility may be expected.

In general paraffins show small internal pressures, increasing with molecular weight and length of chain. The other hydrocarbon constituents of petroleum have greater internal pressures, or more highly developed

dipoles, that also increase regularly with molecular size and length. The asphaltic constituents containing other elements than carbon and hydrogen, principally oxygen, are most different from the lower paraffins and should show the least solubility in the paraffins.

In petroleum, there are representatives of all the hydrocarbon series as well as resins and asphalts in many cases. The proportions of each compound and class of compound vary with different petroleums. Given a particular petroleum, which is a complex solution, the possibility exists of producing such a range of internal pressures by added substances that separation into two layers will occur. This may be done by adding materials of high internal pressure or of low internal pressure. Thus, with a highly asphaltic crude, the addition of pentane, of low internal pressure, will precipitate some asphalt forming a two-phase system. Going a step further and adding propane of even lower internal pressure, there will result a further precipitation of asphaltic bodies and possibly naphthenes or aromatics. This is the principle of

the process of solvent refining of lubricants by propane. The addition of methane is the final step possible. It has the lowest internal pressure of the paraffin hydrocarbons and has no dipole moment. Methane is a gas under normal conditions and its introduction into petroleum requires the application of pressure. In the relation between pressure and solubility of methane in liquids, there is a means of exact and easy control of the quantity dissolved and hence of the range of internal pressures within the liquid. The introduction of methane to petroleum in increasing amount might be expected to produce separation of the compounds of highest internal pressure first, with successive separation of fractions in order of decreasing internal pressure. Theoretically other gases than hydrocarbons would serve also but practically it is doubtful.

Normally, it is hardly to be expected that sufficient gas can be introduced into the petroleum to cause precipitation. In the case of a light petroleum, the solubility is high, but, at high methane concentrations, the transfer of volatile components

from the liquid to the gas phase is large (26). Methane is most soluble in the more volatile components, and as they are transfered to the gas phase with increasing pressure, the proportionality between pressure and gas solubility no longer exists. In fact, the increase in solubility for increments of pressure becomes quite small. Considering a particular two component system such as benzene and methane, at 25°C and four hundred and thirty atmospheres (26), the system is single phase. It may be said that the benzene and gas have become miscible in all proportions. In order to maintain a content of volatile liquids in the liquid phase, it is necessary to add an excess to the original petroleum and limit the extent of the gas phase. This is equally true whether the petroleum is light and contains much volatile material, or heavy and lacking volatile fractions. In the latter case, the solubility of methane is relatively small even at high pressures unless a volatile liquid solvent is added.

From this discussion it is seen that it is theoretically possible to analyse and refine petroleum

by the method of decreasing the internal pressure with methane solution. The use of a solvent promoting a solution of the methane for some petroleums may be necessary.

MATERIALS

Natural gas from the Viking field as supplied to the City of Edmonton was used in this work. The gas has the following composition, (24)

CH_4	90.97
C_2H_6	2.41
C_3H_8	0.58
C_4H_{10} and higher	0.34
N_2	5.70

Traces of sulphur compounds serving as odorants are introduced into the gas before distribution. They have no appreciable effect on the physical behavior of the gas being present to the extent of only six to eight grains per one hundred cubic feet.

As a volatile liquid solvent serving as a diluent for the petroleums used, ligroin, Eastman Practical, was employed. Table I gives the properties of this material. It consists largely of volatile paraffin hydrocarbons.

TABLE I

PROPERTIES OF LIGROIN

Density $\frac{20^\circ}{4^\circ}$ 0.706

Solubility conc. H_2SO_4 2.0%

A.S.T.M. Distillation

I.B.Pt.	68°C	60%	79°C
10%	76	70	80
20	77	80	81.5
30	77.5	90	83.5
40	78	97	87
50	78.5	loss	3%

Two petroleums were used in this work. A composite sample of Turner Valley petroleum was obtained through the courtesy of Imperial Oil Limited from the Calgary terminal of the Royalite Oil Company pipeline from the field. This petroleum was a high grade mixed base oil of paraffinic qualities. Its properties will be given fully in Part II of this report.

The second petroleum used was from Battleview Oils Limited, in the Wainwright field. It was a heavy, black, viscous oil classed as asphalt base. The

properties of this oil are given in Table II. It is highly unstable and readily decomposed by heat.

TABLE II

WAINWRIGHT PETROLEUM

Water	2.55%
Sediment	0.3%
Density $\frac{20^{\circ}}{4^{\circ}}$ (dry)	0.9647
A.S.T.M. (Petroleum as received)	
I. B.Pt.	98°C (water)
2.5%	165°C (First oil drop)
5	203
10	265
20	294 (Cracking commenced)
A.S.T.M. (dehydrated petroleum)	

Cracking commenced before distillation.

The Wainwright crude before being used, was dehydrated. This was done by heating the petroleum in an open bucket to a temperature of 110°C and then holding it at this temperature until all foaming and boiling had ceased. No attempt was made to remove the sediment since it was present in such small quantities.

The Turner Valley petroleum was washed with a twenty per cent sodium hydroxide solution before it was used since the sulphur compounds corroded the valve-seats. The method of washing will be described in Part II. Some of the experiments were carried out on Turner Valley crude oil from which all material boiling below 200°C was removed. This was carried out by an efficient true boiling point column as mentioned in Part II. Further runs were made on material prepared by first dewaxing the crude oil at -29°C and then removing the material boiling up to 200°C in the same column. In one case the light fraction boiling up to 150°C that was removed from the Turner Valley crude oil was used as the solvent for the Wainwright petroleum.

APPARATUS

The apparatus consisted of a compression and storage system, and the equilibrium chamber as shown in figures 1, 2, 3, and 4.

Compression and Storage of Gases

Viking natural gas was compressed in a three-stage compressor, the intake of which was fitted directly to the gas line from the city mains. The gas was pumped into a fifteen litre storage cylinder A (figure1) through valve 8. The pressure in the system could be raised to about four thousand p.s.i. with this compressor. The pressure in cylinder A was indicated on gauge G1. The gas line from the cylinder A led to a four-way junction. With valve 3 closed and valve 6 open, one line from this junction conducted the gas directly to the equilibrium chamber C. A second line from this junction led to a recording gauge G2. This gauge was calibrated against a dead weight piston gauge certified by the National Physical Laboratory, London. The third line from this junction made it possible to fill the five litre cylinder B with gas

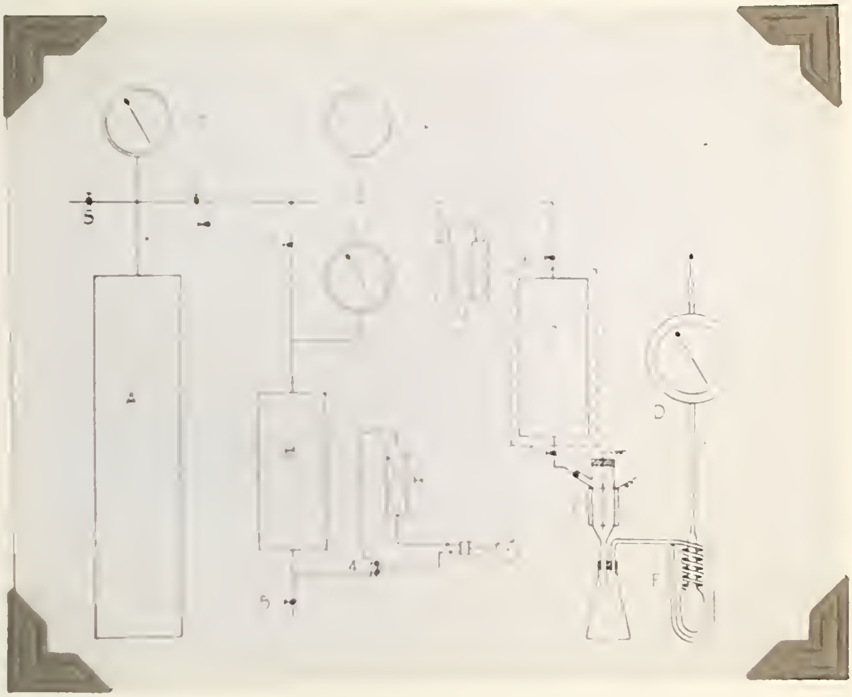


Figure I

Diagramatic representation of the compressor, storage and equilibrium chamber system.

when valve 3 was open. The pressure of the gas could be further increased to five thousand p.s.i. by pumping a fifty per cent glycerin-water solution into the cylinder. Valve 2 was kept closed while the pressure was raised to five thousand p.s.i. The glycerin-water solution used as a fluid piston in the cylinder B, was introduced by a small adjustable hydraulic pump having a maximum capacity of one quart per hour and derived by a half horse-power electric motor. Adjustment of the two-way valve 4 permitted priming of the pump by delivering the fluid to the reservoir H or compression of the gas in cylinder B as desired. The pressure of the gas in cylinder B was measured on gauge G3. When cylinder B was filled with the glycerine solution at the end of a run, the solution was withdrawn through valve 5.

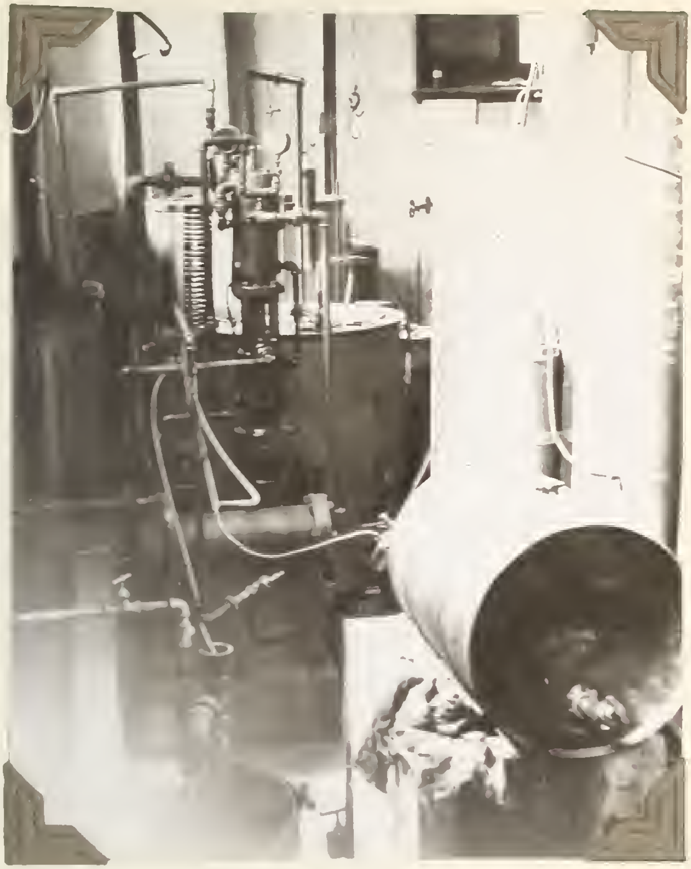
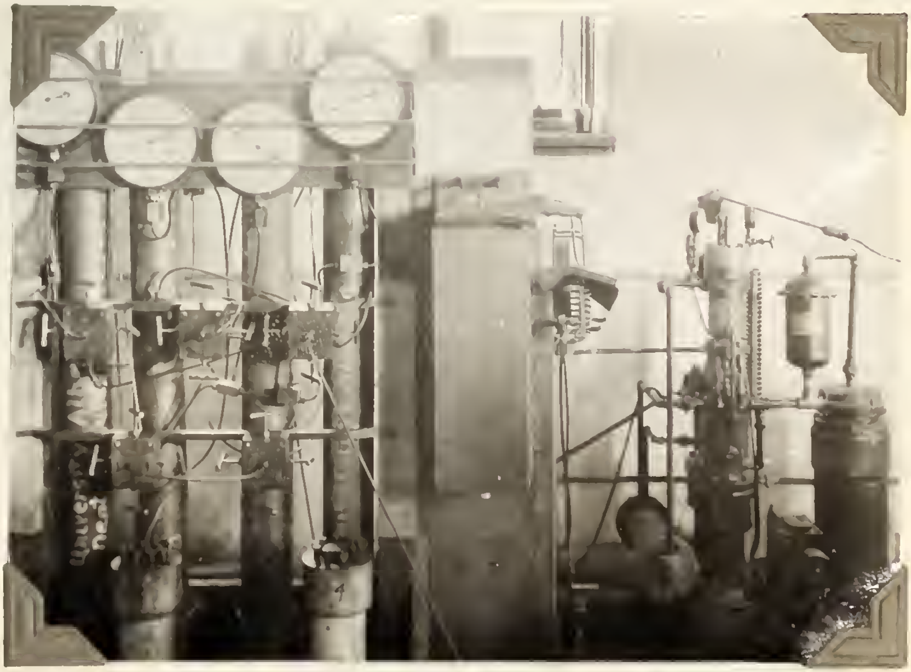


Figure 2

Compression and Storage System



Thus, two methods of compressing the gas in the equilibrium cylinder to the required pressure were available. With valve 2 and 6 open, the pressure could be raised to any pressure up to four thousand p.s.i. using the three stage compressor. For the higher pressures, the whole system was pumped up to four thousand p.s.i. with the three stage compressor by having valves 2, 3 and 6 open. Then with valve 2 closed the pressure is cylinder B and in the equilibrium chamber could be increased to any desired pressure up to five thousand p.s.i. by operation of the hydraulic pump.

The line from the four-way junction to the equilibrium chamber led first to two small pressure bottles G. These acted as liquid traps and prevented any oil that might back up from the equilibrium chamber from getting into the storage part of the system.

The Equilibrium Chamber

This is shown diagrammatically in figure 3 and 4. The reaction chamber was a stainless steel cylinder of five litre capacity. Valve 6 on one end of the cylinder controlled the admission of gas, and valve 7 on the

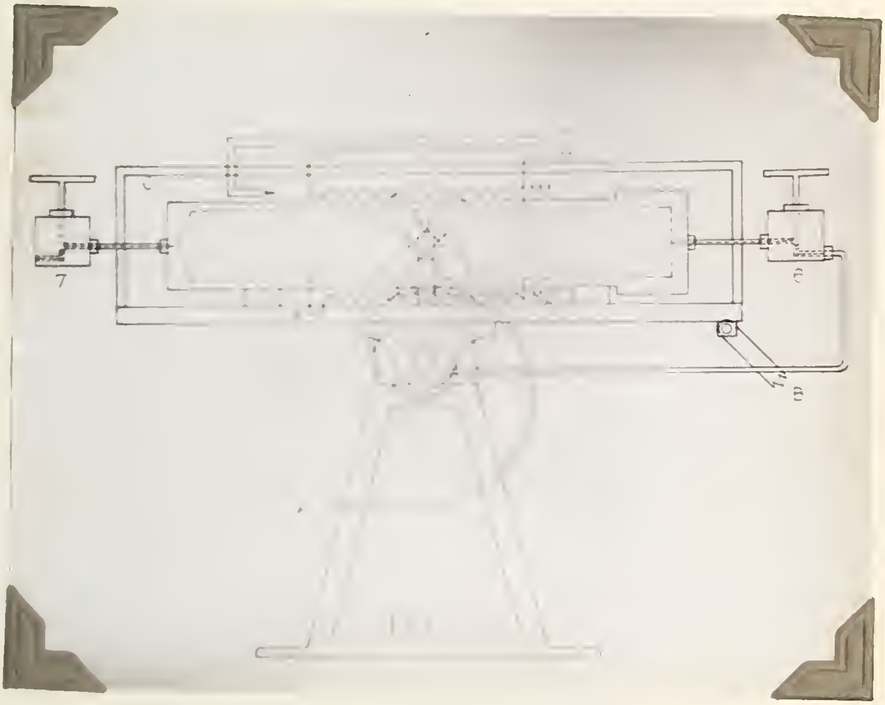


Figure 3

Details of the equilibrium chamber

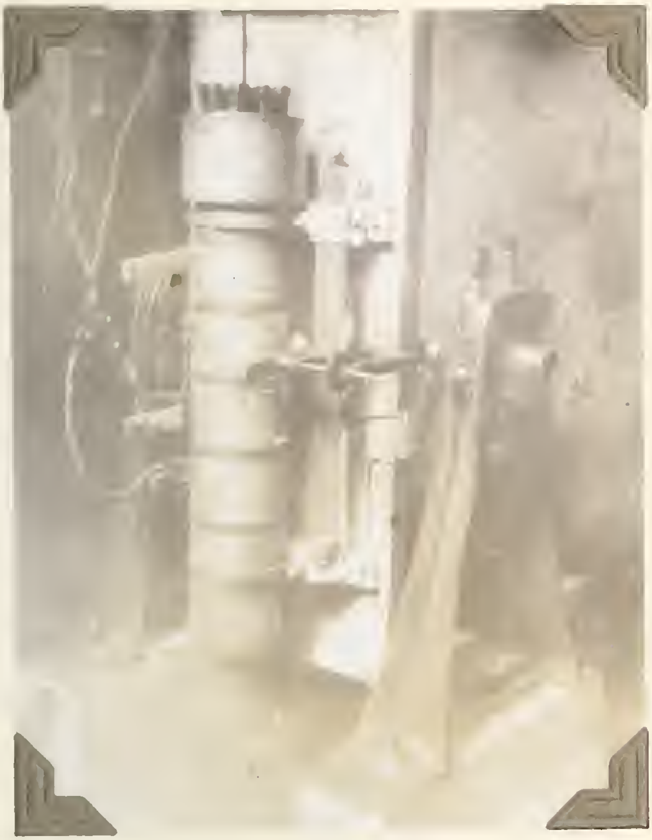


Figure 4

The equilibrium chamber

other end was used for charging and discharging oil. For the first part of the work, a three litre cylinder was used but this volume was found to be unsuitable for the large charges found necessary.

The cylinder was supported on a heavy wooden base-board by means of two strap-iron yokes clamping the cylinder to wooden V blocks fixed to the base-board. The base-board was fixed along its transverse centre line by clamps to a one and a half inch steel shaft. Two standard twenty inch shaft hangers, set journal end up on wooden pillars, supported the ends of the shaft at a height such that the equilibrium cylinder was thirty-five inches above the floor. At one end of the base-board a small wrist pin was attached and a steel connecting rod B linked this wrist pin to another pin on the end of an eight inch crank arm on the slow speed shaft of a reduction gear. In this manner the whole assembly of base-board and cylinder could be oscillated in the vertical plane about the shaft as an axis. The arrangement produced a sixteen inch vertical motion to the end of the base-board, thus rocking it through about 100° between extreme

positions. The reduction gear was driven by a half horsepower electric motor. The apparatus was rocked about forty times per minute. When required the connecting rod could be disconnected and the assembly rotated until the cylinder rested in a vertical position against the wooden stop S.

Control of the temperature of the contents of the equilibrium cylinder was obtained by the use of a thermostatically controlled air bath. Over the cylinder and fitting tightly on to the base-board was a wooden box C lined with a quarter inch asbestos boarding. Inside this box, on one side of the cylinder, a four bladed fan F driven off the rocker motor was attached to the base-board. This fan insured constant circulation of the air in the box and thus an even temperature in all parts. Opposite the fan was placed an electric heater Ml. Also in the box there was an iron-constantan thermocouple connected at T to a potentiometric recording controller. This controller was connected at H to the electric heater. The controller was set at the desired temperature and maintained this temperature in the air bath through an

on-off relay in the heater circuit to ± 2.5°C.

It was not convenient with the equipment available to determine the actual temperature of the contents of the cylinder by an internal thermocouple well. However, in view of the excellent heat conductivity of steel, the outside surface temperature of the cylinder as measured by insulated surface thermocouples served equally well. Attached to the sides of the cylinder were six iron-constantan thermocouples arranged in series. They were placed along the length of the cylinder so that they gave the mean temperature of the whole cylinder. These thermocouples were insulated from the air by asbestos pads. The leads from them passed through a hole in the bottom of the baseboard to the cold junctions maintained at 0°C by an ice-water mixture. The potential created, and thus the temperature of the hot junction was read to 0.2°C on a potentiometer placed beside the apparatus.

Although the temperature of the air bath varied as much as 5°C, that of the cylinder as read from the six-junction thermocouple did not vary more than 0.1°C. This, of course, was to be expected from the relative-

ly great heat capacity of the cylinder and contents compared to that of the air. For temperatures above 25°C, an auxilliary heater M2 was fixed in the box below the fan. This heater could be turned on or off at will by a knife switch K on the side of the baseboard. It was used only for the initial heating of the air bath and cylinder. At the higher temperatures the electrical circuit of the main heater was arranged so that the controlled relay cut out or cut in an external resistance. Thus, the heater was always on but the amount of heat produced changed according to the sign of the temperature variations from the set point.

The discharging apparatus shown in figure I, consisted of a Cottrell electrostatic precipitator E, a condenser F and a wet test gas meter D. The high solubility of natural gas in petroleum at elevated pressures made the use of an electrostatic precipitator necessary. Upon expansion to atmospheric pressure, the evolution of the dissolved gas resulted in some atomization of oil and the formation of a persistent fog. To prevent loss of this oil fog and its passage through

the gas meter the precipitator was placed directly at the end of the discharge tube. The precipitator was made from a glass tube about one and a half inches diameter with a side arm fitting the discharge tube from the cylinder. The tube narrowed down to a three eighth's of an inch glass tube at the bottom of the precipitator. This passed through a rubber stopper fitted to the flask receiving the oil. The one and a half inch tube was surrounded by a sheet of copper foil which made one of the electrodes. A stiff wire fixed in the axis of the tube acted as the other electrode. The precipitator was operated by a twenty-four watt Cox coil operating on a six volt accumulator. The outlet tube from the liquid receiver was connected to a condenser in which the more volatile constituents of the oil were largely recovered from the gas. The condenser was a spiral glass tube wound around and emptying into a cylindrical glass receiver. It was all immersed in an ice-salt mixture in a Dewar flask. The exit from the condenser led to the gas meter.

Softening Point Apparatus

To obtain a qualitative measure of the changing properties of the precipitated asphalt layers, a ball and ring softening point apparatus was used. This was made according to the ball and ring apparatus described in the A.S.T.M. specifications (20). The type used was the tapered ring apparatus made out of brass. The ring had a top inside diameter of eleven sixteenth's of an inch, a bottom inside diameter of five eighth's of an inch and was a quarter inch deep. A three eighth's of an inch steel ball weighing about three decimal fifty grams was used. The ball-centering guide was slightly different from that given in the specifications. The top of the guide had a three eighth's of an inch central hole for the ball and around this were six other one eighth inch holes. The cap was such that the top surface was three sixteenth's of an inch above the top of the ring. The ring was filled by pouring in or pressing in the softened tar using an amalgamated brass plate. The tests were conducted according to specifications. Glycerine was used as the

heating liquid for the higher softening points, and water for the lower ones. The rate of heating was controlled so that it never varied by more than $\frac{1}{2}^{o}$C from the specified rate of five degrees per minute. For the higher softening point determinations the run was started from room temperature, but for those softening points below 60°C it was started from 0^{o}C.

EXPERIMENTAL PROCEDURE

The operation of charging the equilibrium cylinder C with oil was as follows. The cylinder support was freed from the connecting rod to the oscillator gear and rotated until the cylinder was vertical with valve 7 at the lower end. With valve 6 closed, the cylinder was evacuated by a water ejector pump through valve 7 to about one centimetre of mercury pressure. The charge of oil in a weighed closed vessel, the free space of which was filled with natural gas, was admitted through valve 7 into the evacuated cylinder. Natural gas admitted to the oil vessel was allowed to flow after the oil into the equilibrium chamber thus flushing the connecting tubing free of oil and filling the free space in the chamber with natural gas to a pressure slightly lower than atmospheric. Valve 7 was closed. The weight of the oil added was found by weighing the oil charging vessel a second time.

Viking natural gas compressed to four thousand p.s.i. in storage cylinder A was admitted through valves 2 and 6 to the equilibrium cylinder until the

desired pressure was reached and then valve 2 was closed. The cylinder assembly was then rotated to the horizontal position and the connecting rod from the oscillator gear connected to the wrist pin on the base-board. The driving motor was then started and the cylinder oscillated as described previously. The temperature control was set so that the desired temperature as read on the potentiometer was maintained. As heat is liberated when the gas dissolves in the oil, it was necessary in some cases to remove the insulated cover to cool the cylinder to the desired temperature. This was replaced as soon as this temperature was attained. The pressure in the cylinder decreased as the gas dissolved and was maintained by periodic addition of gas through valve 2. The first gas addition was large, and after two or three small additions, equilibrium was reached as shown by constant pressure. The time required for the attainment of equilibrium was generally quite short but oscillation was always carried on for at least one hour.

On the attainment of equilibrium, the connecting

rod was released and oscillation discontinued but temperature control was maintained. If the charge was from Turner Valley crude oil, the cylinder was rotated to a vertical position and allowed to stand in that position for another hour. In the event that two liquid phases were present, this procedure permitted separation into two layers. The discharge tube was then connected to the electrostatic precipitator set in the top of a two hundred and fifty cubic centimetre erlenmeyer flask. About one hundred cubic centimentre portions were removed at a time from the equilibrium cylinder, a new flask being attached to the precipitator for each portion. The oil was weighed and the gas evolved measured each time. During the withdrawal of the charge, the pressure in the equilibrium cylinder was kept constant by allowing gas to enter from the storage cylinder. The gas left in the cylinder after the oil was discharged was then blown off into the air. A density determination was made on each oil sample and the presence of two phases would be evident by a change in density. Two liquid phases were never obtained with Turner Valley

crude oil or its fractions.

This same procedure was tried with Wainwright crude oil and with the Wainwright crude oil dissolved in ligroin, and was not satisfactory. The lower liquid layer was a heavy black tar which was semi-solid at the temperatures of the experiments. This tar tended to block the small one eighth inch pressure tubing which joined valve 7 to the cylinder and further exhibited channeling so that the upper layer came through before all the tar layer was out. The final procedure adopted was as follows. The cylinder, after the contents had been shaken for one hour, was allowed to stand for one hour in a horizontal position so that the lower layer collected along the bottom side. This layer was viscous and adhered to the steel. The cylinder was then rotated a few degrees and held in position by a chain attached to the upper end. The top layer was then discharged through the electrostatic precipitator into a two litre flask followed by the condenser and the gas meter in the usual way. When it was seen by a sudden rush of gas that all the top layer above the outlet pipe was discharged,

the cylinder was rotated a few more degrees and some more of the top layer removed until again there was a sudden rush of gas. This was continued until the cylinder was vertical and all the top layer had been removed. The cylinder was then quickly placed in a horizontal position again before any of the viscous tar escaped. It was found that the heavy layer was completely soluble in benzene and it was a simple matter to remove it from the cylinder as a benzene solution. With the cylinder in the horizontal position, the gas was liberated and a vacuum applied. Approximately eight hundred cubic centimetres of benzene was allowed to enter the cylinder followed by natural gas uŋtil the pressure was about twenty p.s.i. and oscillation was carried out for twenty minutes. The cylinder was then rotated to the vertical position and its contents discharged into a flask. The procedure was repeated using about two hundred cubic centimetres of benzene. This second wash removed traces of tar left in the cylinder and examination showed that the cylinder was clean after this treatment. The benzene was separated from the tar by

distillation. The final distillation was carried out at a pressure of one centimetre of mercury and at a temperature of 125°C. This high temperature was needed to make the tar sufficiently fluid to allow the benzene to escape. The upper layer removed first from the equilibrium chamber was freed of its solvent, ligroin, by distillation at atmospheric pressure until a vapour temperature of 110°C was reached.

When a series of fractions were desired as in runs 19, 20, 22 and 26, the above procedure was repeated at the desired pressures. The initial pressure used was fifteen hundred p.s.i. As described above, at equilibrium the top layer was removed and then the lower or precipitated layer. Each layer was weighed and the top layer, except for a small sample retained, was again charged into the cylinder. The volatile constituents that had condensed in the condenser were added with the top layer. Some of the solvent ligroin was lost due to its volatility at high pressures and subsequent loss on releasing the gas. Since some of the petroleum was removed as a precipitated layer, in each case, balancing to some extent the ligroin loss,

it was assumed that the percentage of ligroin present remained approximately constant. The procedure was repeated at the next higher pressure, two thousand p.s.i. and a second pair of samples obtained. This was done for successive pressures up to thirty-five hundred p.s.i. in increments of five hundred p.s.i. In one case five thousand p.s.i. was applied to the petroleum solution, but the transfer of ligroin into the vapour phase was so great that very little methane went into solution and nothing was precipitated.

The densities and softening points of the precipitated or lower layers were determined; the density by using a Hubbard bottle, and the softening point by using the apparatus described previously. The densities of the upper or oily layer were also determined and an A.S.T.M. distillation was made on each.

RESULTS AND DISCUSSION

The first runs were made on Turner Valley petroleum. The crude oil as received was first charged, and a pressure of three thousand p.s.i. of Viking natural gas applied. The density determinations made on the fractions removed showed no separation into layers. In this run it was found that the sulphur compounds in the crude oil rapidly corroded the valve seats, causing leaks to form, so all the Turner Valley crude oil used in further runs was washed with sodium hydroxide. Run two on the washed crude oil gave no better results with an applied pressure of thirty-eight hundred p.s.i. The lighter material in the crude oil boiling up to 150°C and later up to 200°C was distilled off in a true boiling point column as described in Part II (section on materials) and the residue charged into the cylinder. Several runs at different pressures using this "topped" crude oil were made but were unsuccessful. The next attempts were at increased temperatures, 50°C, 75°C and then 100°C being used with no better results. The pressure

applied was then increased to five thousand p.s.i. using the hydraulic compressor, but negative results were found with both the original crude oil and the "topped" crude oil. Other runs were made on solutions of the crude oil, topped to 200°C and ligroin, using first 50% by weight of ligroin and then 60% ligroin, but no precipitated or second layer was noted. The final attempt was with the dewaxed crude oil, washed, topped to 200°C and dissolved in twice its weight of ligroin. At a pressure of five thousand p.s.i. there was no separation into two layers or precipitate of any kind.

The reason for these negative results lies apparently in the fact Turner Valley crude oil is highly paraffinic containing relatively little naphthenes and aromatics, and no asphalts (14). As was pointed out previously, the internal pressure of the solution must be decreased enormously to cause the precipitation of the aromatics and naphthenes, especially in such low concentrations. Apparently the ligroin was not a good enough solvent for the Viking natural gas to result in a reduction of internal pressure in the

solution sufficiently great to give a separation. As a suitable solvent, a lower paraffin hydrocarbon like propane may serve. This was not attempted because the apparatus would require complete remodeling to provide for handling of the propane solutions and there was not sufficient time for this work to be attempted. The applied pressure of natural gas over a propane solution would not need to be as high as the pressures used over a ligroin solution. Experimental investigation using propane would appear to be desirable and there is every reason to believe that the results obtained would be more promising.

The first attempts on the Wainwright crude oil were made on the crude oil using no solvent. The first run was at a temperature of 25°C and a pressure of three thousand p.s.i. No change in density of the fractions was found. As there was considerable difficulty in discharging the viscous oil, the next run was made at a temperature of 75°C and at a pressure of thirty-eight hundred p.s.i. but nothing resulted. The next two attempts were with the Wainwright crude oil dissolved in the distillate up to 150°C

overhead temperature from Turner Valley crude oil. A solution of forty per cent distillate and sixty per cent Wainwright crude oil and then one of fifty per cent distillate and fifty per cent Wainwright crude oil were tried and no fractional separation was obtained.

A solution of sixty-four point five per cent by weight ligroin and thirty-five point five per cent by weight Wainwright crude oil when charged into the cylinder was found to separate into two layers on addition of natural gas. Solutions of this composition were used in all further experiments. In runs 19, 20, 22, and 26 a fractional precipitation was induced by using successive pressures of fifteen hundred to thirty-five hundred p.s.i. gage pressure in five hundred p.s.i. increments as described in the section on experimental procedure. The experimental data obtained from the analysis of the fractions produced and the average values are shown in Table 3.

This table gives the weight of the charge, the weight per cent, density in grams per cubic centimetre , and softening point in degrees centigrade of the pre-

cipitated layer for each pressure. The pressures tabled are corrected values.

TABLE 3

Upper and Lower Layers From Wainwright Crude Oil After Removal of Solvents

Pressure, lbs per sq. in.		1595	2120	2634	3120	3660
	Run No.					
Upper Layer; weight %	19	94.0	91.3	89.2	87.9	87.0
	20	93.7	91.0	87.7	85.3	83.9
	22	92.6	89.1	85.8	82.8	84.0
	26	91.2	88.0	84.5	82.2	80.6
	average	92.9	90.2	87.4	84.8	82.4
Lower Layer; weight %	19	6.0	2.7	2.1	1.3	0.9
	20	6.3	2.7	3.3	2.4	1.4
	22	7.4	3.5	3.3	3.0	2.4
	26	8.8	3.2	3.5	2.3	1.6
	average	7.1	2.7	2.8	2.6	2.4
Softening Point °C	19	129	104	99	79	70
	20	109	103	87	69	54
	22	103	115	96	78	54
	26	104	115	102	78	53
	average	116	107	96	78	54
Density; gr/ccm.	19	1.094	1.057	1.110	1.087	1.055
	20	1.099	1.083	1.073	1.059	1.050
	22	1.087	1.063	1.069	1.067	1.053
	26	1.095	1.087	1.075	1.059	1.050
	average	1.095	1.083	1.072	1.062	1.050

Run No.	19	20	22	26	average
Final upper layer;					
Density, gr/ccm.	0.918	0.886	0.904	0.920	0.907
Cracking temp. °C	369	330	313	333	338

Note: "Average" values are read from the graphs of the data in Figures 5 and 6.

The densities and softening points are plotted agains the pressures of natural gas used on the graph shown in figure 5, and the amount of oil in the upper layer as a percentage of the original crude oil at each pressure is plotted on the graph shown in figure 6. The product from the upper layer will be called refined oil, and that from the lower layer, precipitated. As is seen, the experimental points do not agree very well with themselves. The probable reasons for the large discrepancies between the data of duplicate runs, together with suggested improvements will be discussed later.

From the properties given, it is seen that a true fractionation was obtained. The properties, densities and softening points show a definite change with the increased external pressures. Both the softening points and the densities decrease regularly, the average of the determined values especially of the densities, fall on a straight line. It would be expected that these cruves would tend to flatten out at the higher pressures but the pressures used here do not seem to be high enough to exhibit this. The regular variation with pressure of the properties suggests that the crude

oil that would be precipitated are those with the highest internal pressures and most unlike the paraffin natural gas added. These will be the carbenes which in a Soxhlet analysis are those insoluble in carbon tetrochloride but soluble in benzene. These have the highest densities and molecular weights of the asphaltic constituents. They are solids at room temperature. Then the asphaltenes and asphalt-resins would come out in turn, these have a lower gravity and are semi-solids at room temperature. These asphaltenes and asphalt resins are described as those fractions which are insoluble in paraffinic solvents but soluble in carbon tetrachloride. A more comprehensive study of the fractions would have been obtained if a complete Soxhlet analysis had been made on the precipitated fractions and if also an ultimate analysis had been carried out. It would also have been helpful to determine the molecular weights of these precipitates. From the data thus obtained, molecular weights and ultimate analysis, a method of determining the actual components of the oil might be obtained. The first pressure used should have been about 500 p.s.i. and a wider fractionation would have been obtained. In the first fraction that was

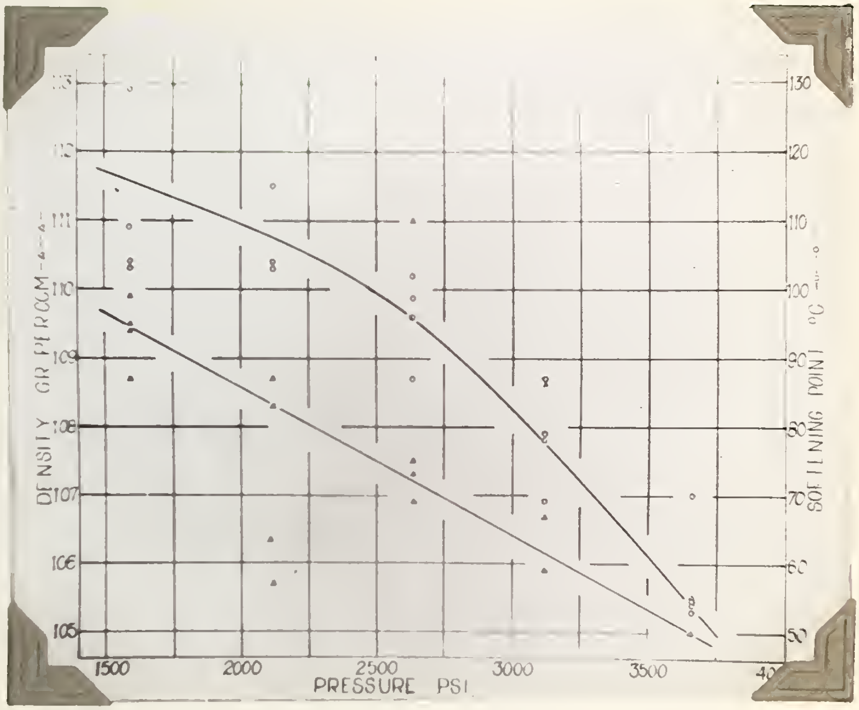


Figure 5

Properties of the precipitates

Density —△—

Softening Point —⊙—

obtained at fifteen hundred p.s.i. there was probably considerable variety in the compounds precipitated.

Since the precipitation of the fractions depends upon the decrease in internal pressure, it would be very helpful if the change in the internal pressure of the natural gas-ligroin solution could be obtained. The data from which the internal pressures may be calculated (21), heats of vaporization, expansion and compressibility data, etc. are not available for such a solution as was used. The method of obtaining internal pressure too are not very accurate. If this internal pressure data were obtained, then the relation between the precipitated layers obtained in the manner outlined in this investigation and those fractions obtained from a Soxhlet analysis could be found.

The graph of refined oil against pressure in figure 6 also shows a fairly uniform slope. It is seen from it that the amount precipitated is about two point six per cent for each increment of five hundred p.s.i. in the pressure applied. This is in accordance with the assumptions that equal increments in pressure of gas, i.e. solubility of gas, produce proportional decreases in

internal pressure and a complete series of compounds of differing internal pressure occur in the oil.

In table 4 the results of an A.S.T.M. distillation of the refined oil are listed. Whereas the original dehydrated crude oil could not be distilled without cracking, over forty per cent was distilled over from the refined oil before cracking of the constituents commenced. The distillate obtained too was water-white until about thirty per cent has come over. This is an important result and not altogether expected, that removal of a relatively small portion of heavy complex compounds from a crude oil would result in marked differences in the material left.

Since all these properties, densities and softening points decreased as the internal pressure of the solution decreased, then a true fractionation was obtained by the modification of the solvent with pressures of natural gas. This shows also that there is a theoretical basis behind the empirical separation of asphalts etc. into resins, asphaltenes, carbenes and carboids by the use of different solvents. But as yet the division into these different classes of compounds

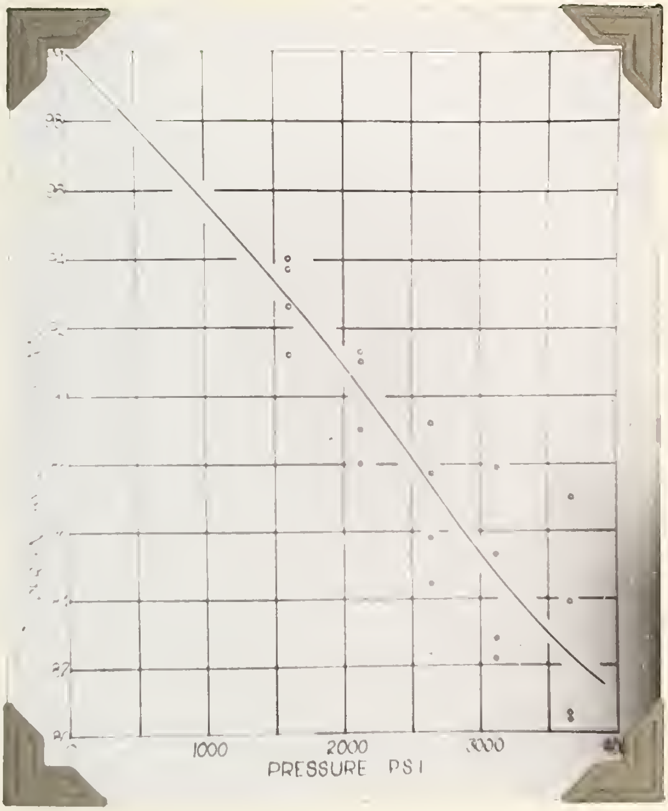


Figure 6

Per cent of refined crude oil in the upper layer.

TABLE 4

A.S.T.M. Distillation on Refined Oil

Run No.	19	20	22	26
Bar. Pres.	705.8 mm	696.8 mm	700.8 mm	700.8 mm
I.B.P.	114.5°C	112.0°C	107.0°C	113.0°C
10%	141.0	150.0	129.8	152.0
20	205.0	228.5	175.0	261.5
30	369.0*	312.5 *	289.0*	308.0 *
40		325.0	313.0	322.0
% Yield before cracking	32	41	42	45
Cracking temp. °C	369.0	330.0	313.0	333.5

* Slight coloration of distillate.

has not been made standard. Because of the true fractionation obtained, this procedure provides an excellent method of analysis, and if the internal pressures can be determined, a basis for standardization exists. Many modifications will be necessary to obtain absolutelyreproducable results, but these can be found with further experimental work.

The errors in this investigation are very apparent, but the lack of reproducibility of results is due mainly to a lack of an absolute standardization of the methods used which would follow after further investigation. Some of the methods might have to be abandoned. The chief difficulties are in handling the fractions after they have been obtained in the benzene solution, and the removal of the solvent ligroin from the upper layers. Asphalts are very subseptible to oxidation and their properties are very easily changed. The distillation to remove the benzene must be absolutely standard and would probably give better results if carried out in an atmosphere of some inert gas like nitrogen. It is possible that another solvent would be better or even a different technique. Referring to

figures 5 and 6, the reproducibility of results increased as the softening point decreased. This was probably due to the easier and more complete removal of the benzene at lower temperatures from the materials of lower softening point. The precision of the density measurements was increased as the softening point was lowered. There was less chance of occlusion of bubbles of benzene vapour in the density samples from the materials of lower softening point. It is possible that the required information as to amount and properties of the precipitate could be obtained without removing the benzene used as the solvent. This would require considerable improvement in technique and the development of testing methods that may also be difficult. The upper layer caused much less trouble than the lower layer. The material in the upper layer was quite fluid and relative to the lower layer, stable to heat and oxygen. The ligroin was removed easily as described and there was no difficulty with density measurements or A.S.T.M. distillations.

Another possibility of reducing the difficulties in treating the tar substances would be the preliminary

removal of the heavy tars which are solids at room temperature by using a solvent that gives an initial precipitation. This would also provide one with an extra fraction. The layers that would precipitate out in the cylinder upon the application of the pressures of natural gas would then all be liquids and the properties and analysis of such a liquid layer would be more easily conducted.

In making comparisons between the experiments in a series of increasing pressure, the assumption has been made that the loss of ligroin and the precipitate removed in each experiment balanced one another. Thus it was assumed that the concentration of ligroin in the oil in the cylinder was constant in a series of experiments. This assumption is probably in error, though not of much importance in work of a preliminary nature. The problem could be solved readily by analysis of a sample of the upper layer before starting the next experiment of a series and adjusting the ligroin concentration accordingly.

These experiments, of an exploratory nature have shown that the solubility of the components of Wainwright

crude oil, asphaltic in character, in a light hydrocarbon solvent, ligroin, may be controlled by the solution of methane under pressure. The properties of the solvent may be controlled at will by the pressure and hence the solubility of the gas, to produce a series of precipitated fractions. Expressing the influence of the dissolved gas on the solvent in terms of internal pressure, it may be said that a series of fractions of increasing internal pressure may be obtained by continuously decreasing the internal pressure of the solvent or environment in the solution. The possibility of an accurate and simplified method for obtaining fractions of crude oil of regularly varying properties by fractional separation by selective solvents is indicated. The products obtained from this separation are unchanged from their original conditions when present in the crude oil and thus a more accurate analysis is possible. That this method of refining a crude oil can be extended to commercial applications is also very probable. The removal of relatively small amounts of the more complex compounds, generally termed asphalts, from the crude oil leaves a refined oil of markedly different properties from the original crude oil.

Summary

In this investigation, preliminary experiments on a method of analysis of crude oil through fractional precipitation by the modification of a solvent with dissolved natural gas are described. The results indicate that such a procedure is quite possible but how far this process can be applied is yet to be determined. From the negative results on the Turner Valley petroleum it is apparent that this method is not applicable to all types of crude oils without some modification. That the use of propane as the solvent is the modification necessary to give the desired results is suggested and further work with this appears desirable.

From the properties of the fractions that were determined, a true fractionation is obtained by this method and a selective removal of the constituents is indicated. The use of such a method for analysing and refining petroleums is indicated and it is hoped that further work will lead to a simplified and reliable procedure.

PART II

The equilibrium phase compositions in systems of a composite Turner Valley Crude Oil and Natural Gas.

INTRODUCTION

This investigation as previously stated is preliminary work to a more extensive and precise examination of the products of crude oil wells in Turner Valley.

The knowledge of the behavior of complex hydrocarbon systems under equilibrium conditions corresponding to those found in underground petroleum reservoirs is of primary importance in the efficient handling and control of production in oil and gas fields. The presence of the more volatile hydrocarbons in solution contributes energy to help in forcing the oil through the porous sands to the well and through the tubing to the surface. It also causes a lowering of the viscosity and surface tension of the oil thus allowing better drainage from the capillary pores and better freedom of movement in the sand channels. Thus with efficient control of the gas content of a producing

oil horizon, the ultimate recovery of the oil is increased. There results also a longer period of flowing life and so a more economical production. The amounts of gas produced per barrel of oil is also decreased. Knowledge of the solubility of natural gas in crude petroleum and of the changes in properties resulting from the presence of the gas is of importance in deducing the nature of the processes taking place in underground formations, in estimating underground reserves, and in arriving at a system for controlling petroleum production in a given field.

There is also another important reason for the need of solubility data on natural gas-crude oil systems. The design of modern equipment is becoming more accurate and this requires data of a greater accuracy than is given by the use of the ideal gas laws commonly used heretofore. The use of high pressure equipment in the processing of crude oils is becoming more common and in the design of this equipment the relation between the temperature, pressure, and composition of two coexisting hydrocarbon phases is essential. At pressures of not over forty to sixty p.s.i. Raoult's

and Dalton's law can be used to calculate the P.T.V. data with sufficient accuracy for engineering purposes but as the pressure are increased, the deviations of the calculated values from the actual also increase and become quite large. Extensive and accurate data is needed to develop a modified form of these laws using fugacity instead of pressure.

The study of vapour-liquid equilibria in hydrocarbon systems in this laboratory was undertaken with the view of its application to the Turner Valley oil field. The work in the laboratory was started in 1932 by Argue (2) and continued from 1934 to 1936 by Johnson (26). Piercy (35) continued the work from 1936 - 1938. This investigation, together with that of Hugill and Gillies (25) is a continuation of this work.

LITERATURE REVIEW

There has been little investigation into the complex hydrocrabon systems such as occur in petroleum until recent years. A little work was done in 1926 by Mills and Heithecker (34) who examined the solubility of natural gas in various crude oils. They proved that the volume of the oil increased and the specific gravity decreased in proportion to the amount of gas dissolved. In 1926, Beecher and Parkhurst (4) published the results of work on the solution of gases in crude oil. They examined solutions of carbon dioxide, air and hydrogen in addition to solutions of several natural gases in Oklahoma crude oil. They found that the amount of dissolved gas in crude oils varied directly as the pressure at any temperature. This is of course in accordance with Henry's law that "a given quantity of liquid will dissolve at constant temperature, quantities of the gas which are porportional to the pressure of the gas. "They also determined the viscosity of the solutions and related this property with the frictional resistance to the flow of oil through sands. They

found further that the surface tension of the crude oil was reduced by dissolved gas. Dow and Calkin (15) published about the same time the results of a very similar work using air and natural gas solutions in Wyoming and Oklahoma crude oils. Lindsly (33) in 1931 reported work on the solubility of natural gas in crude oil more or less under field conditions by obtaining samples of solutions at the existing well head pressure. Also in 1931, Frolich et al. (17) investigated the solubility of methane in several separate hydrocarbons. They state that Henry's law is followed over a wide range of pressure if the gas does not form a chemical compound with the solvent. They also state that the solubility may be considered a linear function of the absolute pressure, depending on how well the solute obeys the perfect gas law. If deviations from the gas law are applied, the straight-line relationship holds at high pressures.

Beginning about 1931, a number of independent and comprehensive investigations into the physical properties of hydrocarbon systems were commenced. Sage and Lacey et al. (40) published the first of a series of

papers entitled "Phase Equilibria in Hydrocarbon Systems" in 1934. The methane-propane system is described in the second of their series (41). They also studied the solubility of propane in two types of crude oils (47) giving changes in viscosities, the partial heat of solution and the heat evolved in such systems. In the third of their papers (30) they describe a methane-crude oil system. In this paper they reach the following conclusion that "the assumption that a simple dissolving process occurs when a gas is brought to equilibrium with a liquid in complex hydrocarbon systems is valid only when the system is far enough below the critical temperature of the solvent and the critical temperature of the mixture that there is no appreciable transfer of the components of the original liquid phase into the gas phase". They also come to the conclusion that "The solubility of a dry natural gas in a given crude oil at 100°F is almost directly proportional to the saturation pressure." In a further paper, Sage, Backus and Lacey (43) studied the methane-crystal oil system over the temperature range 70° to 220°F and at pressures up to three thousand p.s.i.

In this, measurements were made of the total volume of the system of known mass as a function of pressure, temperature, and composition. In studying solutions of methane and propane in crystal oil (47), they showed the effect of the dissolved gases on the viscosity. They have published many papers since this last one reviewed, dealing mainly with the solutions of pure constituents in two or three component systems.

In 1932, Brown, Saunders and Smith (9) published papers dealing with the pressure-volume-temperature relations of paraffin hydrocarbons. They apply the data that they have obtained in the design of process equipment.

Also in 1932 and 1933 Lewis and Luke (31, 32) published data on the volatility of hydrocarbons at temperatures below their critical temperature in the presence of noncondensable gases at high pressures. Their work at that time was with nitrogen and benzene but they were extending this investigation into the natural gas - crude oil systems.

Katz and Hachmuth (28) describe a crude oil-natural gas system in which they determine the equili-

brium constant, K, for the systems at pressures up to three thousand p.s.i. and temperatures from 40° to 200°F. The equilibrium constant K is described as the ratio of the mole fraction of a constituent in the vapour phase to the mole fraction of that constituent in the liquid phase at a defined temperature and pressure. The region of retrograde condensation is readily shown in the graphs of the equilibrium constant versus the pressure in p.s.i.

The work in this laboratory on "Phase Equilibria in Hydrocarbon Systems" was started by Boomer and Argue in 1931 (2). The investigation of a number of two component systems have been carried out by Boomer, Johnston and Piercey (6,7,8) dealing with methane as the solute, and pentane, hexane, heptane, cyclohexane, methyl cyclohexane, benzene, and toluene as the solvents. At present work is also being carried on with the natural gas-naphtha system (25).

MATERIALS

Viking natural gas as described in Part I was used for this work. Its composition and density were given in that section.

The crude oil used was a composite Turner Valley oil as delivered at Calgary by pipe line from the field. Our thanks are due to the Imperial Oil Company Limited for their courtesy in providing us with this material. The properties of this crude oil are given in Table 5.

TABLE 5

Properties of Turner Valley Crude

Density $\frac{20^\circ}{4^\circ}$ 0.8077

A.S.T.M. distillation, barometer 701 mm.

5%	73.0°C
10	89.0
20	124.0
30	153.0
40	188.0
50	236.0
60	277.0
70	328.0 (Cracking started)

The petroleum was distilled in an efficient true boiling point column. The distillation curve obtained is shown in Figure 7. At 225°C the pressure was reduced to forty milimetres Hg, when 200°C was reached at forty millimetres Hg, the pressure was further reduced to ten milimetres Hg. When the temperature again reached 200°C the distillation was stopped and the residue removed and placed in a vacuum still with a short fractionation g column. The pressure in this column was reduced to one millimetre and the distillation carried to completion. The percentage over and the corresponding temperatures together with the refractive index and density of the cuts will be found in Appendix I of this report.

As the crude oil contained corrosive sulphur compounds it was washed with a twenty per cent sodium hydroxide solution before use. The sodium hydroxide solution was placed in a five foot length, one and a half inch diameter glass tube which was filled with small lengths of three sixteenth's of an inch glass tubing. The oil was placed in a funnel at the top of a long tube leading into the bottom of the column.

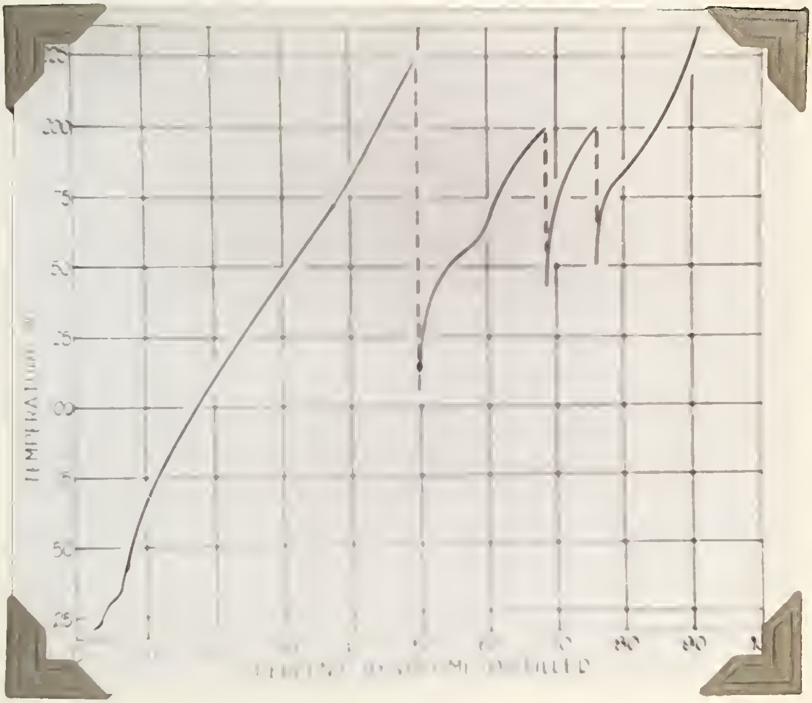


Figure 7

True Boiling Point Curve of

Turner Valley Crude Oil

The funnel was held at a height of about one foot above the top of the column to provide sufficient head to force the crude oil into the column. The crude oil rose through the sodium hydroxide solution, effective contacting being caused as it passed through the packing of the glass tubes, and overflowed from the top into a forty litre drum. This material was used directly in the experiments described.

APPARATUS

The apparatus consisted essentially of the gas compression and storage system, the equilibrium chamber, the expansion train, and auxilliary equipment for determining the properties of the phases.

1. Compression, Gas Storage and Equilibrium Chamber

The gas compression and storage system and the equilibrium chamber is the same as that described in Part I and shown in Figures I, 2, 3, and 4. The method of operation and of discharging was changed.

The volume of the equilibrium cylinder was determined by weighing the water required to fill it. It was found to be five thousand and six point five cubic centimentres. The volume of cylinder B (Figure I) and the system up to valves two and six was also measured. This was done by measuring at atmospheric pressure the volume of Viking natural gas that was contained in the system when it was at a pressure of five hundred and ten p.s.i. From the expanded volume of gas, and using the deviations of Viking natural gas from ideality as found by Johnson (26), the volume of the system was found to be fifty-six hundred and eight cubic centimetres.

2. Discharge Apparatus and Expansion Train

Samples of the two phases were collected in two steel pipettes (A Figure 8) in a manner to be described. These sample pipettes were steel pressure bottles with valves 9 and 10 fitted to each end. The volumes of these two pipettes were separately determined by weighing them empty and then weighing them filled with mercury. The volume of the gas sample pipette was found to be one hundred and sixty-seven point fifty-six cubic centimetres and that of the liquid sample pipette was one hundred and fifty-five point fifty-six cubic centimentres.

The expansion train is shown in figure 8. The sample pipette A was clamped to the wall by two steel brackets. The discharge fitting of the pipette passed through a rubber stopper set in the entry tube of a glass water-cooled condenser B. The end of the metal discharge tube extended about one and a half inches below the stopper to prevent the oil from coming in contact with the stopper. The outlet tube of the condenser led through another rubber stopper into a weighed glass bulb C of two hundred anf fifty cubic

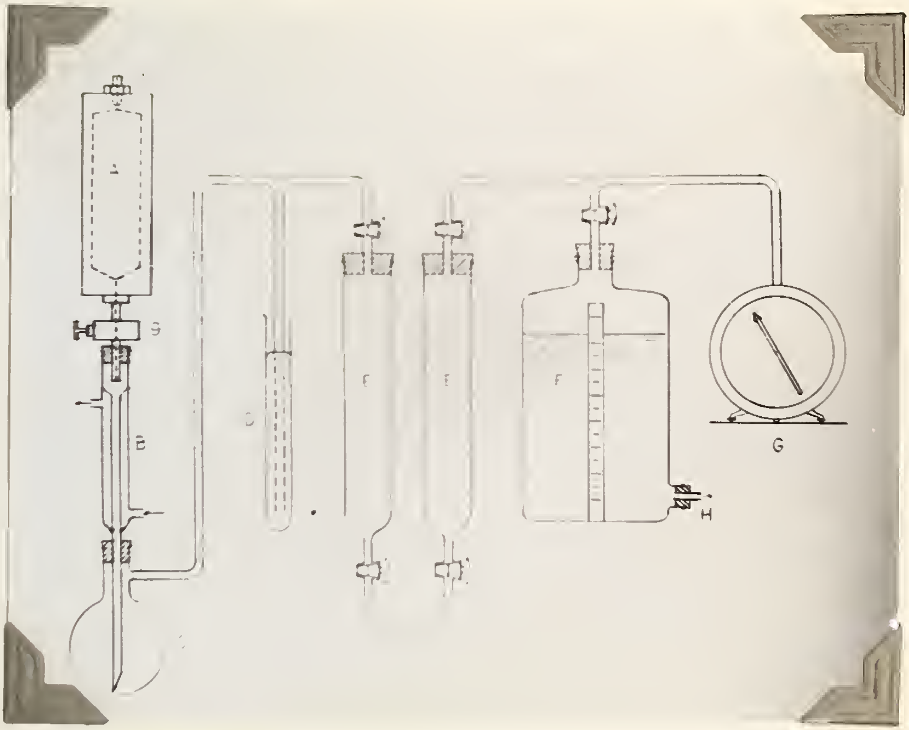


Figure 8

Expansion Train

centimetres capacity. A side arm connected on the neck of the flask served as the outlet for the gas. This outlet was connected by rubber tubing to a T joint. One arm of this joint was connected to a glass tube which was immersed to a depth of about five inches in mercury held in a long test tube D. This acted as a safety valve to prevent any breakage due to a sudden release of gas under pressure. The gas was then led through two charcoal absorbers E arranged in series. These were one and a half inch glass tubes with a rubber stopper and a stopcock of capillary bore at one end, the other end being sealed directly to a capillary stopcock. These were filled with activated charcoal. From these the gas passed through another T joint, one arm of which led to a calibrated gas sampling bottle F. Here a continuous sample of gas was collected over water during discharging of the pipettes. The water passed through H into a similar bottle which acted as a reservoir. Connection was made from the other arm of the T to the wet-test gas meter G.

3. Auxilliary Equipment

Fractionating Column - To determine at least approximately and on a comparative basis the change in composition of the crude oil as a result of an experiment, a small fractionating column and still were used. The still and receiver were fitted through ground glass joints to the column. The column itself was made from fourteen-millimetres of glass tubing, the walls of which were indented with alternating hemispherical depressions and drip points over the whole length. This tube was surrounded by a silvered glass vacuum jacket. A thermocouple well filled with heavy oil was fitted at the top of the tube at the level of the vapour off-take line. The vapours were condensed in a small water cooled condenser from which a return line fitted with a stopcock led to a drip point within the column just above the vacuum jacket. The condenser outlet was also connected to the receiver immersed in an ice-water cooling mixture. The amount of oil which went back as reflux was controlled by the stopcock placed in the reflux line. The receiving flask was a cone shaped one hundred cubic centimetres graduated centri-

fuge tube and the initial thirty cubic centimetres of of distillate could be measured quite accurately. The still was of two hundred and fifty cubic centimetres capacity. It was heated by a bunsen burner and protected from air currents by a surrounding metal shield. The overhead temperature was recorded by a two junction iron-constantan thermocouple using a cold junction set in ice and water kept in a Dewar flask.

Charcoal Distillation Apparatus - The apparatus used in the recovery of gases and liquids from the activated charcoal was a modification of that described in code 101, American Gas Association (1). It consisted of a steam boiler, charcoal stripper, condenser and receiver. The steam was led to the bottom of the charcoal bed in the stripper through an internal axial tube and rose through the charcoal to escape through a top outlet tube to the condenser. An external electric heater brought the temperature of the steam and charcoal to 300 - 350°C. Experience showed this procedure more satisfactory for present purposes than the glycerine distillation specified in Code 101. The vapours passed from the stripper into an ice cooled condenser

and the condensate was caught in a receiver also surrounded by an ice bath as specified in Code 101. The water and oil layers were separated in this receiver and the volume of the oil layer was measured to point one cubic centimetres. This accuracy of measurements was not satisfactory in some experiments where the volume of the liquid condensate was of the same order of size.

EXPERIMENTAL PROCEDURE

The procedure in this series of experiments may be considered conveniently in two stages. There was first, the acquiring of samples of the gas and liquid phases in equilibrium and second, the examination and analysis of these samples.

Preparation of Phase Samples

The equilibrium cylinder was charged with oil as described previously in Part I. At each pressure two separate experiments were made differing only in quantity of oil used. The weights of the oil charges used were eight hundred and seventy-five grams and seventeen hundred and fifty grams, i.e. ten hundred and eighty-three point five cubic centimetres and twenty-one hundred and sixty-seven cubic centimetres. These quantities were chosen in order to provide data showing the effect of differing gas-oil ratios on the equilibrium phases present.

After adding the oil to the cylinder, gas was added in known amount by use of the following procedure. The whole system excepting the equilibrium

cylinder was brought to three thousand p.s.i. The temperature of the compression cylinder B and of the other parts of the system was noted. Valve 2 was closed and valve 6 was opened, gas being admitted to the equilibrium chamber to the desired pressure. If the contents of cylinder B were insufficient to bring the system to the required pressure, glycerine-water solution was pumped in until the desired pressure was reached. This pressure was maintained until equilibrium was reached as described previously in Part I.

Upon the attainment of equilibrium at 25°C, the cylinder was turned to its most vertical position with the discharge end, valve 7, up. The gas sample pipette, which had been previously evacuated to one millimetre pressure, was then attached to the cylinder by a short length of steel tubing between valves 7 and 9. Then while the pressure was kept at the desired pressure by expanding gas through valve 3 or by pumping in glycerine solution, valve 7 and 9 were slowly opened and a sample of the gas phase allowed to expand into the pipette. By having the discharge end of the equilibrium cylinder up, the gas which is added to maintain constant press-

ure must bubble through the oil when entering the cylinder. The volume of gas added was small and it was assumed that the gas reached equilibrium with the liquid phase and the concentration difference in the phase before and after sampling was negligible. Since the gas sample was taken from the top of the cylinder very little if any of this newly added gas would enter the pipette. When the pipette was filled, valves 7 and 9 were closed and the pipette removed.

To ensure that equilibrium had been established with the added gas, the cylinder was again shaken for one hour. In calculating the results, the total volume of gas including that removed in the gas sample pipette was assumed to be in contact with the oil. At the end of the hour, the cylinder was again stopped and set vertical, this time with the discharge end downward. Then the liquid sample pipette which had previously been filled with mercury, was attached in the same manner as the gas sample pipette. Then since the pipette was filled with mercury, valves 7 and 9 could be opened fully. Keeping the pressure in the cylinder constant, or slightly above the equilibrium pressure,

by expansion of gas through valve 2, valve 10 was opened and the mercury allowed to run out. This method of obtaining the liquid sample was necessary in order to prevent liberation of any dissolved gas from the liquid phase with consequent error in sampling. Any reduction of pressure would release gas in the liquid phase and a true liquid phase sample would not be obtained. When all the mercury had been discharged, any excess pressure of the gas in the system was released by expansion of the gas through valve 1. Valves 10, 9, and 7 were closed and the liquid pipette was dettached. Valve 6 was then closed and the remaining material in the cylinder was discharged through valve 7. The pressure of the gas in the remainder of the system was brought back up to three thousand p.s.i. i.e. the initial condition, by pumping the glycerine solution into cylinder B. The temperature of this cylinder was again noted. The glycerine in cylinder B was discharged through valve 5 into a five litre flask, joined to the discharge tube by a rubber stopper, and its volume measured. The volume of gas that was dissolved in the solution was measured by passing it through a wet-test gas meter. The

volume of dissolved gas was found in each case to be negligable and so no account was taken of it in the calculations. Knowing the volume of glycerine used, the temperature change , if any, during the experiment, and the deviation of Viking natural gas from the ideal gas laws from previous work (26), the quantity of gas added to the equilibrium chamber could be calculated.

Analysis of Samples

The phase samples were expanded separately, the gas sample usually first while the contents of the equilibrium chamber were attaining equilibrium prior to taking the liquid sample. The sample pipette was placed in the brackets as described previously. With the gas phase sample, no condensable fractions collected in the liquid receiver (C Figure 8) but it was used to serve the purpose of a surge tank in reducing the effect of occasional sudden rushes of gas. Previous to connecting the activated charcoal absorbers, they were flushed with Viking natural gas and weighed. After completing all connections in the train, Viking natural gas was passed through to displace air and then the reading of the gas meter was noted.

Expansion was carried out slowly to atmospheric pressure by carefully opening valve 9. In passing through the activated charcoal, all of the pentanes and heavier vapors together with some of the lighter constituents were stripped from the gas. After one litre of gas had passed, sufficient to flush the train, the stopcock to the gas sample bottle was opened and a continuous gas sample taken during the rest of the expansion. The final reading of the gas meter, the volume of the gas sample, and the temperature and pressure were noted. In order to recover pentanes left in the gas in the sample pipette at one atmosphere pressure, connection was made through valve 10 with the Viking gas supply and the system was flushed with one litre of the gas.

The stop-cocks on the charcoal absorbers were closed and they were weighed, the increase in weight representing absorbed gas and vapors. The charcoal was then placed in the distilling cylinder of the steam distillation apparatus and superheated steam passed through it for one half hour. The liquid sample collected in the receiver was assumed to be all pentane and

its volume was measured. For purposes of calculation, the gases, methane, ethane, propane and butanes absorbed in the charcoal were taken as being propane.(15a)

The density of the gas sample collected was determined using a gas density bulb. The gas was expanded into the evacuated bulb and then allowed to come to room temperature and then to atmospheric pressure by opening the stop-cock momentarily to the atmosphere. The temperature of the water in the gas sampler was noted to enable a correction for the weight of water vapour present in the gas to be calculated.

The liquid sample was treated in a similar manner. In this case the liquid receiver also was weighed before and after the discharging of the pipette. The specific gravity of the liquid recovered was measured at 20°C with a hydrometer. The volume of the sample was also measured. One hundred cubic centimetres of this liquid was then placed in the fractionating column and a distillation carried out using maximum reflux in the column. The treatment of the dissolved gas liberated was as described previously for the gas phase sample.

RESULTS AND DISCUSSION

The experimental conditions and extensive quantities for this investigation are given in Table 6. Pressures are gauge pressures and volumes are measured at 25°C and seven hundred and sixty milimetres mercury. The data under "liquid sample" and "gas sample" are on the whole material taken in the sample pipettes described previously. Inspection of Table 6 will show that for each pressure, two different quantities of oil were used, thus providing some information concerning the influence of gas and oil ratio on the results. Attention is drawn to the data for the pentane recovered from the charcoal. This quantity was measurable only to decimal zero five cubic centimetres and consequently large errors are possible, particularly with the gas phase at low pressures. The experimental data of Table 6 was used in the calculation of the specific properties of the system.

The specific properties and other quantities derived from the direct experimental data are shown in Table 7. The phase densities were calculated from the masses of the phase samples and the volumes of the

sample pipettes. They are probably accurate to decimal two per cent in the case of the liquid phase and decimal five per cent in the case of the gas phase. The phase volumes were calculated by means of a weight balance using the data of Johnson (26) on Viking gas to compute the mass of the gas added from its pressure, volume and temperature. These quantities are no more precise than the phase densities. The remainder of the data is self-explanatory. The expression of phase compositions as shown is arbitrary. All condensate from the charcoal distillation described previously is called pentane and all gases from the charcoal, computed as propane. The gaseous material in the charcoal is however, only a small part of the total gas. The principal error appears in the data on pentane. An error of as much as decimal one cubic centimetres is possible and probably decimal zero five cubic centimetres error is common. As a consequence, little significance can be attached to the pentane data for the gas phase in runs ten to thirteen inclusive. The data means merely that there was some pentane, greater than decimal zero five cubic centimetres but less than decimal one cubic centimetres in amount.

Table No. 6
EXPERIMENTAL DATA

Expt. No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Gauge Pressure p.s.i.	2634	2634	2634	2634	2634	2120	2120	1595	1595	1065	1065	510	510
Vol.oil chgd.(ccm)	1083	1083	1083	2167	2167	1083	2168	1083	2168	1083	2168	1083	2168
Wt.Oil chgd.(gms)	874.4	874.7	874.9	1750.2	1750.2	875.1	1750.7	875.1	1750.9	875.1	1750.8	875.1	1750.8
Vol.Gas $\frac{25^\circ}{760\text{mm}}$ (ccm)		986,900	994300	829,600	811,100	809,800	662,400	628,300	391,700	393,400	341,500	191,800	170,300
Wt. Gas (gms)		690.2	705.5	588.6	575.5	574.6	470.0	445.8	277.9	279.1	242.3	136.1	120.8
Liquid Sample													
Wt.Oil (gms)	99.46	99.94	99.63	98.84	96.03	101.93	102.20	105.40	105.11	110.23	110.73	115.97	116.30
Wt. in Charcoal(gms)	4.11	4.65	4.76	4.99	5.06	5.22	4.80	5.00	4.60	3.89	2.57	2.76	2.85
Vol.Pentane (ccm)	3.0	2.5	2.5	3.0	3.1	3.0	2.9	2.8	1.7	2.2	1.2	1.7	1.7
Vol.Gas (ccm)	13,880	13,630	13,370	13,180	13,320	10,180	11,230	8720	8800	6090	6140	3040	2870
Wt.Gas (gms)	9.66	9.13	9.15	9.12	9.25	7.09	7.77	5.90	6.07	4.16	4.26	2.14	1.98
Gas Sample													
Wt. in Charcoal(gm)		1.47	2.21	1.55	2.64	1.10	1.78	1.00	1.10	0.84	0.33	0.37	0.85
Vol. Pentane (ccm)	1.0	1.47	1.5	1.2	2.0	0.9	0.8	0.3	0.3	0.1	0.1	0.1	0.1
Vol. Gas (ccm)	38090	36430	35490	34390	34210	28,890	28,660	21,400	20,800	13,000	13,810	5,810	5,830
Wt. Gas (gms)	26.70	25.54	26.13	25.48	23.83	20.96	20.61	15.04	14.55	8.06	9.90	4.08	4.11

Table No. 7
PROPERTIES OF THE PHASES IN EQUILIBRIUM

Exp. No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Press. p.s.i.	2634	2634	2634	2634	2634	2120	2120	1595	1595	1065	1065	510	510
Vol.charge ccm	1083	1083	1083	2167	2167	1083	2168	1083	2168	1083	2168	1083	2168
Liq.Phase Dens. gms/ccm		0.7310	0.7299	0.7261	0.7089	0.7340	0.7378	0.7476	0.7443	0.7603	0.7557	0.7770	0.7787
Liq. Phase Spec.Vol - $\frac{1}{d}$		1.368	1.370	1.377	1.410	1.362	1.355	1.337	1.344	1.316	1.323	1.287	1.284
Gas Phase Dens. gm/ccm		0.161	0.169	0.161	0.1579	0.1316	0.1336	0.0957	0.0934	0.0531	0.0611	0.0266	0.0296
Gas Phase Spec.Vol $\frac{1}{d}$		6.203	5.916	6.199	6.333	7.573	7.480	10.449	10.72	18.83	16.37	37.59	33.78
Vol.Gas Phs.ccm		3889	3914	2509	2435	3897	2641	3906	2799	3929	2759	4009	2879
Vol.Liq. " "		1284	1259	2664	2738	1276	2532	1267	2375	1244	2414	1164	2294
Gas Phs/Liq.Phs.		3.029	3.109	0.941	0.889	3.054	1.043	3.083	1.179	3.158	1.143	3.444	1.255
Comp. Gas Phase													
Butanes& Lighter ccm		36700	36200	34840	34980	29140	29370	21850	21330	13430	13960	5980	6270
gms		26.07	27.40	26.28	25.22	21.40	21.89	15.85	15.49	8.84	10.17	4.39	4.90
Pentane&Heavier ccm		1.5	1.5	1.2	2.0	0.9	0.8	0.3	0.3	0.1	0.1	0.1 -	0.1 -
gms		0.94	0.94	0.75	1.25	0.56	0.50	0.19	0.16	0.06	0.06	0.06	0.06
Gas-oil ratio in Gas Phs.ccm/ccm		2.45×10^4	2.41×10^4	2.90×10^4	1.75×10^4	3.23×10^4	3.66×10^4	7.27×10^4	8.51×10^4	13.39×10^4	13.95×10^4	5.97×10^4	6.23×10^4
Comp. Liq. Phase													
Gas Recovered ccm		15260	15090	14910	15050	12040	12890	10520	10770	7490	7150	3990	3870
gms		12.21	12.24	12.23	12.37	10.43	10.75	9.15	9.61	6.67	6.08	3.84	3.77
Liquid Recovered ccm		124.5	124.5	124.0	122.1	128.0	127.9	132.8	131.2	138.2	137.7	144.7	145.2
gms		101.51	101.20	100.72	97.97	103.81	104.02	107.15	106.17	111.61	111.48	117.03	117.36
Gas-oil Ratio in Liq. Phs.ccm/ccm		1.23×10^2	1.21×10^2	1.20×10^2	1.23×10^2	0.94×10^2	1.01×10^2	0.79×10^2	0.82×10^2	0.54×10^2	0.52×10^2	0.28×10^2	0.27×10^2

The ability of the experimental procedure to duplicate experiments is illustrated by the pairs, experiments 2 and 3, 4 and 5, differing only in gas-oil ratio. Referring to Table 6, the discrepancies between the data within a pair is as high as three per cent. This is much greater than the errors in the measurements on one experiment. The discrepancy in duplication must be attributed to two things, the precision with which the pressure gauge will duplicate correctly a required pressure, and the certainity with which a true sample is obtained. It is highly probably that the system is in equilibrium and that the technique used will produce true samples. Hence it is felt that the discrepancies between duplicates are due largely to inability to reproduce pressure readings. The gauge is probably reproducible to one per cent of its reading which would account for the errors bearing in mind the effect on both phases.

The phase densities are shown graphically in Figure 9. Evidently, changing the relative volume of gas and oil in the system within the limits used, about two to one ratio, and within the experimental error,

has no effect on the phase densities. One would predict an increasing density for the liquid phase with increasing gas-oil ratio at constant pressure and temperature because of the increased transfer of the light components from the liquid to the gas phase. At any one pressure, the liquid phase density would approach a maximum as the gas-oil ratio approached very large volumes. These effects would be shown only by more precise work. The effect of changing the gas-oil ratio on the gas phase would be comewhat different. With increasing gas-oil ratio, the phase density would change only slightly, if at all, until an appreciable part of the higher components had been removed from the oil. Beyond this, the addition of more gas would give a reduction in the phase density, the density approaching in the limit the density of Viking gas. The two density curves in Figure 9 slope in opposite directions and apparently will coincide at sufficiently high pressures. It is not probable, in view of the high boiling material in the oil, that the system will show a critical or consolute pressure.

The volume of the liquid phase increases with increasing pressure. This is explicable on the basis of

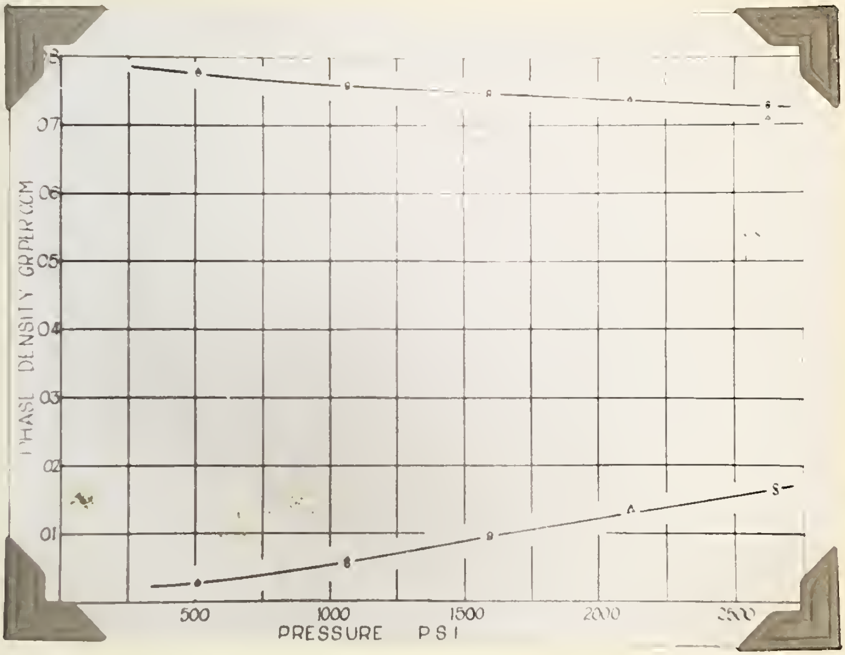


Figure 9

Phase Densities in the Equilibrium Chamber

Gas Phase/Liquid Phase 3.1:1 —⊙—

" " " " 1.1:1 —△—

the increasing amounts of gas dissolved with increased pressure. Although volatile constituents of the liquid are transferred to the gas phase in increasing amounts with increased pressure, the increased amounts of the dissolved gas more than counteracts the effect. It is probable, and has been observed in previous work on simple systems, that with sufficiently small initial gas phase, increasing pressure would result in the disappearance of the gas phase. The volume ratios of the phases in the equilibrium chamber are as expected. In both cases, the gas-liquid ratio decreases slowly with increasing pressure, i.e. the volume of the liquid phase increases while the volume of the gas phase decreases with increasing pressure.

It has been shown elsewhere (4, 33, 34) that along with the decreasing density in the liquid phases, there is a corresponding decrease in the viscosity. Evidently, in order to promote the rapid and easy flow of oil through the porosities in a producing formation, as much gas should be retained in solution as is practicable.

Turning to the phase compositions, the most interesting results are those showing the transfer of material

from the liquid phase to the gas phase. The Viking gas is free from all but traces of hydrocarbons heavier than methane, but at equilibrium the gas phase has a higher density than Viking gas at the same pressure. This is shown by the following data on densities.

Pressure, p.s.i.	510	1065	1595	2120	2634
Phase density	0.0275	0.0605	0.0950	0.128	0.161
Viking gas density	0.0264	0.0581	0.0918	0.1245	0.1547

The phase densities have been takes off an enlarged graph of Figure 9 and are graphical averages. The values for the density of Viking gas are from Johnson (26). This transfer of material from the liquid to the gas is also shown directly in the pentane content of the gas phase. The pentane content of the gas phase shows a minimum concentration around one thousand p.s.i. pressure and increases with higher or lower pressures. This is to be expected and has been demonstrated frequently with other and simpler systems (26). In the limit, at atmospheric pressure, the vapour content of the gas will be high and dependent on the vapour pressures of the volatile constituents in the crude oil.

In applying these results to the Turner Valley field, it must be pointed out that the gas and oil used

here are not quite the same as found in the field. The gas is deficient in higher hydrocarbons and the oil is deficient in lower hydrocarbons. Since the pressure of higher gaseous hydrocarbons in the gas phase promotes the transfer of material from the liquid phase to the gas phase, the pentane content found here is smaller than might be expected under comparable conditions in the field. Data on the Turner Valley field in its earlier stages of development is scanty and only approximate figures can be given with regard to the naphtha wells. It is probable that the pressures were in the neighborhood of two thousand to twenty-five hundred p.s.i. and the product of the wells was between decimal twenty-five and decimal five gallons of naphtha per one thousand cubic feet of gas (12). This corresponds to a gas-oil ratio range of twenty-four thousand nine hundred to twelve thousand four hundred and sixty cubic centimetres of gas per cubic centimetres of naphtha. The temperatures in the producing horizon are not well known but are around 25°C (39A). Comparing these figures with the experimental gas-oil ratios in Table 7, the agreement is as good as can be expected. Currently, the pressures in the naphtha region of the

field are much lower, being only three hundred to one thousand p.s.i. and the gas-oil ratio very much higher, corresponding to, on the average, one million cubic centimetres of gas per cubic centimetres of naphtha. This is again in general agreement with the experimental results but suggests that equilibrium does not now exist in the naphtha producing areas in the Valley. Referring to Figure 10, it is seen that the ability of the gas to hold vapours decreases with decreasing pressures to a minimum. The course of events in the productive formation, as the pressure dropped, may be visualized as a progressive condensation of naphtha in the formation. Consequently the gas removed from the wells will contain less naphtha vapours. At sufficiently low pressures, one thousand p.s.i. or less, increased yields of naphtha should result, but this has not been observed in continuously operated wells. Apparently contact between the remaining gas and the naphtha is not sufficiently good or of long enough duration to yiel equilibrium conditions. Generally, a decrease in gas-oil ratio is observed in shut-in wells, an observation that could be predicted as a result of an approach to equilibrium conditions.

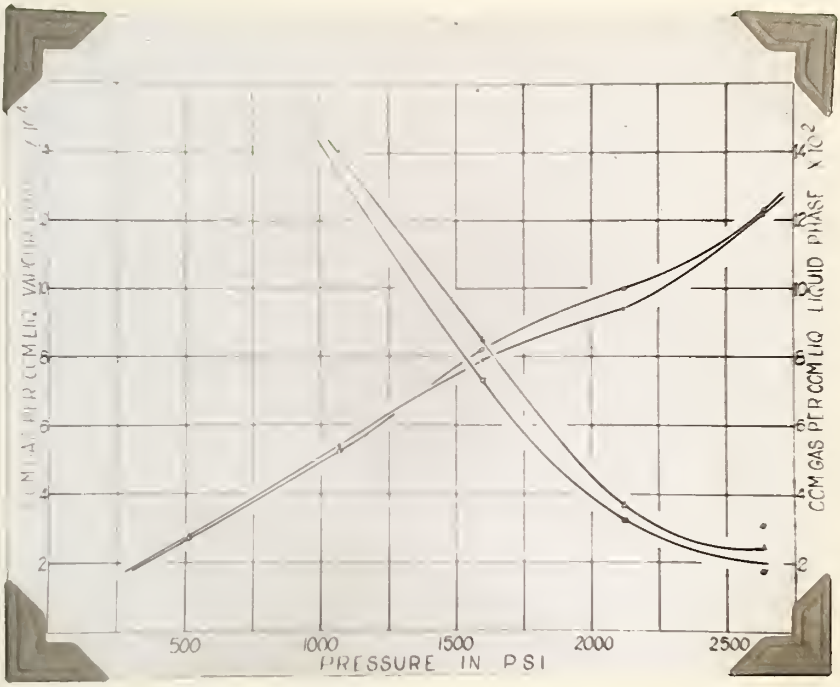


Figure 10

Gas-oil Ratio in the phase Sample

Liquid phase oil over all gas-oil ratio 3.1 —x—
" " " " " " " " 1.1 —⊙—
Gas phase over all gas-oil ratio 3.1 —⊙—
" " " " " " " 1.1 —△—

The results of these experiments suggest that the original state of the materials in the naphtha producing formation was a gas phase. The fact that comparable gas-oil ratios are obtained in the laboratory using a Turner Valley crude oil to saturate the gas suggests also that the production from the naphtha wells originates in a gas cap above the crude oil. In other words, there is a connection between the formations producing crude oil and those producing gas. The writers are not competent to discuss the geologic features that may confirm or disaffirm this view. The observed slow increase in pressure in shut-in naphtha wells may be due to pressure equalization in the sands immediatly adjacent to a well or, in the light of the above discussion, may be due in part to flow of gas from the oil sands to the naphtha sands.

In the application of these results to operations in the field, it is obvious that the highest recoveries of naphtha are obtained at the highest pressure. In short, pressure conservation should be practiced. In addition, the rate of the pressure drop should be kept at a minimum in order that the naphtha condensed in the formation during the pressure drop be given opportunity

to remain in equilibrium with the gas; thus the highest possible naphtha concentrations in the gas corresponding to the pressure are obtained. Operating a naphtha well at or even near its capacity is very poor practice from the point of view of ultimate recovery of naphtha. It should be practiced only if combined with a process of repressuring; the gas after being stripped of naphtha being returned to the formation in adjacent wells. Given sufficient data on the gas composition, pressure and temperature, the time to reach equilibrium in the formation, and the economics involved, the most advantageous rate of gas flow in any area can be estimated. Such a procedure, while leading to the most economic recovery of naphtha, will, on the assumption that the gas phase is in connection with the crude oil phase, conserve pressure and gas so essential to the highest recoveries of crude oil.

The data given in Table 7 with regard to the liquid phase are of interest principally in their relation to the behaviour of the gas phase. The value of gas in solution under pressure in crude oil is generally admitted and conservation is generally practiced so far as is

Table No. 8

FRACTIONAL DISTILLATION DATA ON OILS

Expt. No.	Original Crude Oil	1,2,3	4,5	6	7	8	9	10	11	12	13
Pressure p.s.i.		2634	2634	2120	2120	1595	1595	1065	1065	510	510
Gas Phase / Liq. Phase		3.067	0.965	3.054	1.043	3.083	1.179	3.158	1.143	3.444	1.255
2.5%	42.3 °C	72.0	66.4	67.3	66.6	64.0	63.0	57.6	54.6	54.0	52.6
5.0%	58.4	84.7	82.8	82.8	82.0	77.0	79.5	77.0	71.1	69.7	69.0
7.5%	72.1	93.8	92.2	91.7	90.6	86.7	90.2	88.5	84.5	82.3	79.7
10.0%	83.4	104.0	100.0	99.1	99.0	96.4	99.7	98.8	94.0	93.1	88.8
12.5%	93.4	113.5	109.0	110.5	107.8	103.0	107.4	105.0	103.5	101.6	99.6
15.0%	102.9	123.0	116.0	118.4	115.0	113.3	114.8	113.0	110.0	109.2	108.4
20.0%	121.0	140.4	134.0	135.4	135.0	131.6	133.4	131.0	126.6	124.4	124.6
% over at 150°C	27.8	23.0	24.3	24.0	24.4	24.3	24.6	25.0	26.0	26.7	27.0

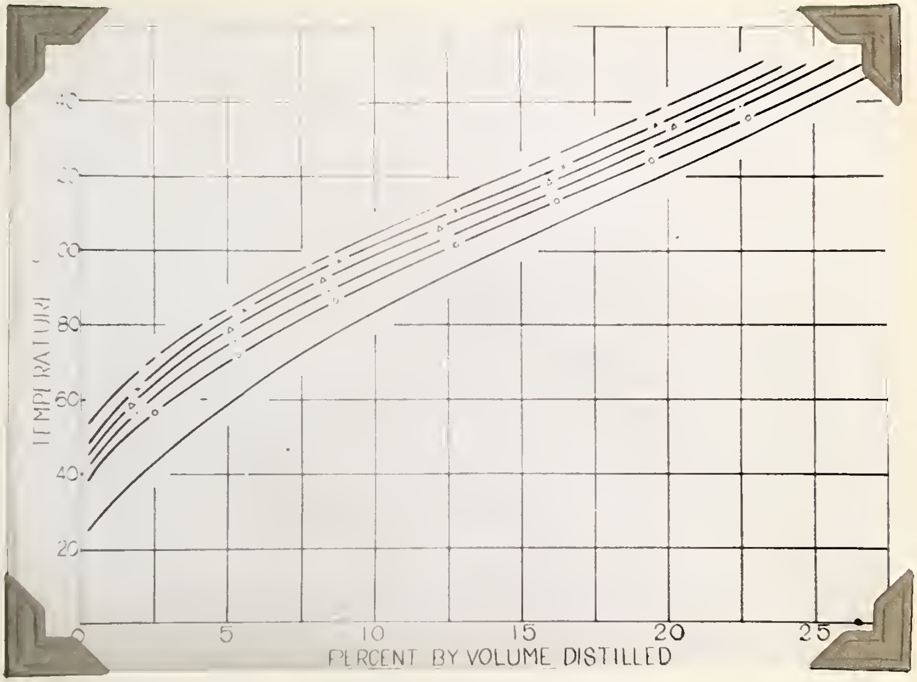


Figure 11

Distillation Curves for Oil from Liquid Phase

Gas-oil ratio 7.1
Original ————
500 p.s.i. —— ○ ——
1000 p.s.i. —— • ——
1500 p.s.i. —— △ ——
2000 p.s.i. —— × ——
2500 p.s.i. —— — ——

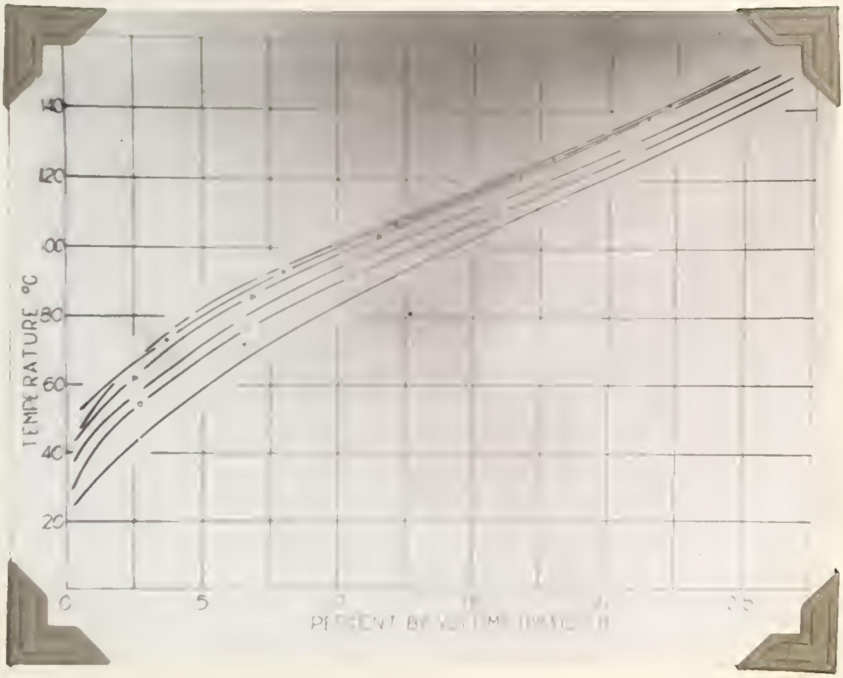


Figure 12

Distillation Curves for oil from

Liquid phase, gas-oil ratio 1.1

Original	———
500 p.s.i.	—○—
1000 p.s.i.	—•—
1500 p.s.i.	—△—
2000 p.s.i.	—×—
2500 p.s.i.	— - —

economically feasible.* The solubility of natural gas in crude oil has been shown many times (17,30) to follow Henry's Law up to moderate pressures with negative deviations at the higher pressures. This is found to be true in the present case by inspection of the gas-oil ratios and Figure 10. The gas was liberated from the oil in the manner described previously and no attempts were made to standardize the rate or temperature. Consequently only qualitative conclusions can be drawn from the vapour content of this gas. Due to the approximate establishment of equilibrium between the oil and gas at atmospheric pressure the vapour content is much higher than that found in the gas phase. This vapour content upon condensation corresponds to casing-head gasoline in the field. It will be related to the vapour or pentane content of the gas phase in equilibrium only in so far as

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* The dissolved gas reduces the density and viscosity of the oil and upon the liberation of the gas in the formation, provides the driving force necessary to lift the oil to the surface. The time during which the well will flow without the use of pumps and the ultimate recovery of oil is increased by gas conservation.

the gas phase depletes the oil phase of lighter liquid hydrocarbons.

That the crude oil used in these experiments loses volatile materials to the gas phase is demonstrated by the distillations given in Table 8 and shown in Figures 11 and 12. The transfer of material from oil to gas in increasing amounts with increasing pressure is clearly shown and corresponds with the results discussed in connection with the gas phase composition. The amount transferred is relatively greater at the low pressures and an upper limit appears to be approached as the pressure is increased. The effect of differing relative volumes of gas and liquid phase is seen on comparing Figures 11 and 12. As expected, there is a greater transfer of material from the oil to the gas, the greater the gas volume relative to the oil volume. That the gas phases show much the same composition in both cases, merely means that in the proportions used here, there is much more than enough volatile material in the oil to saturate the gas.

SUMMARY

Apparatus and methods required to bring a Turner Valley crude oil and Viking natural gas into equilibrium in two phases at various pressures was described.

Assuming that conditions in the producing formation of Turner Valley are an oil phase in contact with a gas phase, and neglecting the influence of the producing sand, conditions existing in the field have been reproduced approximately in the laboratory.

The solubility of natural gas in crude oil increases approximately proportionally with increasing pressure.

The density of the liquid phase in equilibrium decreases and its volume increases with increasing pressure. The density of the oil recovered after the removal of the dissolved gas is greater than that of the original crude oil. Distillation of the oil recovered shows it to contain an increasingly smaller proportion of volatile material as the pressure is increased.

The density of the gas phase increases with pressure and is always greater than the density of Viking natural gas at the same pressure. Amounts of pentane and higher hydrocarbons are found in the gas phase that

vary with pressure, increasing rapidly at the higher pressures.

Transfer of the volatile constituents of the crude oil to the vapour phase in amounts depending upon the pressures, has been demonstrated.

The results have been applied to the Turner Valley field in a qualitative way. The correspondence between laboratory and field data suggests that the naphtha wells in the Valley are fed by a gas cap above the crude oil area, or by a gas phase in connection with the crude oil area.

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APPENDIX I

PROPERTIES OF FRACTIONS OF TURNER VALLEY CRUDE OIL

The Turner Valley crude petroleum was fractionated in an efficient true boiling point column as stated previously in the section on materials in Part II. The volume, density and refractive index of the fractions were determined. Cuts number 16, 17 and 18 were solids at 20°C and therefore the refractive index could not be determined on the pure fractions. Solutions of varying compositions of these cuts in kerosine were made and the composition and refractive index determined for each. The refractive index of the pure component was then found by extrapolation of the curve of refractive index versus composition to zero concentration of kerosine. The data are presented in Table 9.

From the determination of refractive index and density, the compositions of the lower boiling fractions can be determined by a method described by Kurtz and Waddington (29). A very complete examination of a composite Turner Valley crude oil, and some data on other Alberta oils have been reported by Donald (14). The chemical and physical properties of narrow cuts and estimates of composition are given.

The distillation data are shown graphically in Figure 7, Part II. The crude oil yields about forty-five per cent as straight run gasoline, and ten to fifteen per cent kerosine. The gas oil and heavier fractions contain much wax and have comparatively high cloud points. The oil is relatively stable to heat and the fractions obtained were colour stable and did not form gums on standing.

Table 9

PROPERTIES OF FRACTIONS OF TURNER VALLEY CRUDE

Cut No.	%	Temp. °C	Press.	Density $\frac{20}{4}$	Refractive Index $\frac{20}{0}$
Gas	2.18				
1	8.61	57.4	701mm	0.6309	1.35030
2	14.99	93.2		0.7055	1.39601
3	21.85	114.4		0.7427	1.41596
4	28.29	137.0		0.7613	1.42727
5	35.38	165.8		0.7777	1.43721
6	41.48	185.4		0.7882	1.44205
7	50.07	225.0		0.8037	1.44901
8	53.96	148.4	40mm.	0.8238	1.45960
9	57.78	157.0		0.8344	1.46642
10	61.56	174.8		0.8406	1.47027
11	65.49	188.0		0.8424	1.46977
12	68.98	200.0		0.8482	1.47254
13	72.97	182.2	10mm.	0.8650	1.48183
14	76.53	200.0		0.8764	1.48964
15	80.51	180.8	1mm.	0.8766	1.48878
16	84.51	193.6		0.8829	1.49190
17	88.50	215.6		0.8913	1.49800
18	92.49	251.3		0.9046	1.50638
19	100.00	Residue		0.9385	

Extrapolation of refractive index of kerosine solutions to zero concentration.

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